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Dolomite—magnesian calcite relations at elevated temperatures and CO_2 pressures*

Donald L. Graf† and Julian R. Goldsmith‡

(*Received November* 1954)

ABSTRACT

The equilibrium thermal decomposition curve of dolomite has been determined up to a CO_2 pressure of 20,000 lb/in.², at which pressure dolomite decomposes at 857°C. Equilibrium was approached from both directions, by the breakdown and by the solid-state synthesis of dolomite.

At elevated temperatures and pressures, calcites in equilibrium with periclase as well as those in equilibrium with dolomite contain Mg in solid solution. In the former, the Mg content increases with increasing CO_2 pressure, and decreases with increasing temperature. In the latter, it is a function of temperature only. The exsolution curve of dolomite and magnesian calcite has been determined between 500° and 800°C; at 500° dolomite is in equilibrium with a magnesian calcite containing ~6 mol per cent $MgCO_3$; at 800°, ~22 mol per cent. There appears to be a small but real deviation from the ideal 1 : 1 Ca : Mg ratio of dolomite, in the direction of excess Ca, for material in equilibrium with magnesian calcite at high temperature.

The experimental findings indicate that very little Mg is stable in the calcites of sedimentary environments, but that an appreciable amount is stable under higher-temperature metamorphic conditions, if sufficient CO_2 pressure is maintained.

Introduction

A knowledge of the thermal behaviour of dolomite and of the general equilibrium relations in the system CaO—MgO—CO_2 is of considerable significance to sedimentary and metamorphic petrology. Very little equilibrium work has been done in this system, although a considerable number of investigations on the (non-equilibrium) behaviour of dolomite and calcite during differential thermal analysis have been carried out.

In 1923, Mitchell attempted to determine the equilibrium thermal decomposition curve of dolomite, at rather low pressures, by heating dolomite and measuring the CO_2 pressure developed. Haul and Markus (1952) computed a curve, but were forced by the lack of thermochemical data on dolomite to treat it as a "mixture" of calcite and magnesite. Nevertheless, their values indicate that Mitchell's CO_2 pressures at all temperatures were much too low, which suggests that he had not obtained equilibrium decomposition.

The present paper deals with the results of an experimental investigation of that portion of the system CaO—MgO—CO_2 from 0 to 50 mol per cent $MgCO_3$. The equilibrium thermal decomposition curve of dolomite is presented, and the equilibrium relations of magnesian calcites at elevated temperatures and CO_2 pressures are elucidated.

Experimental Procedure

Approximately 10-mg quantities of the initial carbonate materials were enclosed in platinum foil and reacted in cold-seal pressure vessels of Haynes Alloy No. 25, modified after the type described by Tuttle (1949). Pressures up to approximately

* A portion of this material was presented at the 1953 meeting of the Geological Society of America, Toronto, Canada.

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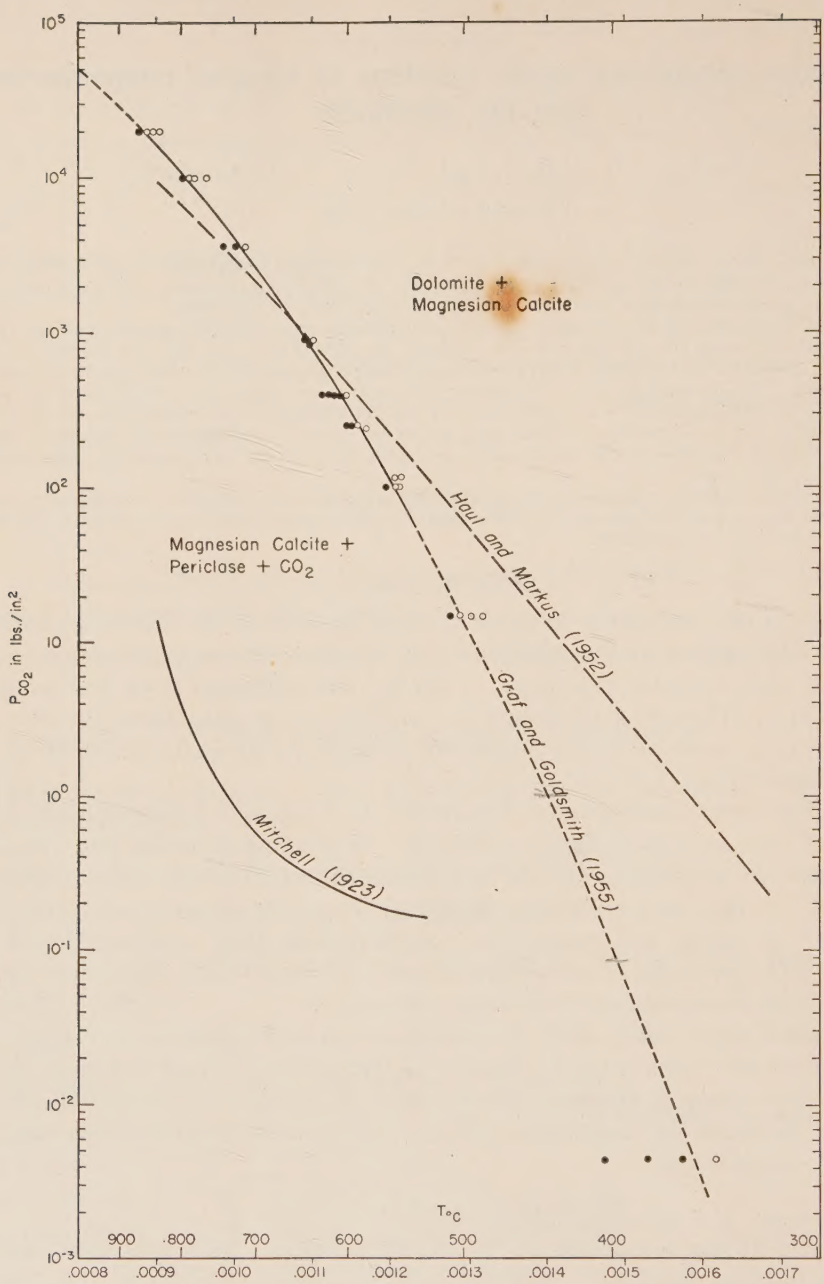

Fig. 1. Equilibrium thermal decomposition curve of dolomite plotted as $1/T°_K$ versus log P_{CO_2}, based on runs using dolomite as starting material. Open circles—no decomposition observable; filled circles—some decomposition observable. The experimental data of MITCHELL (1923) and the calculated curve of HAUL and MARKUS (1952) are shown for comparison.

1,000 lb/in.^{2} were obtained by direct connection of a CO_2 cylinder to the pressure vessel. A valve in the line to the cylinder was then closed, the pressure vessel heated to the desired temperature, and the pressure bled back to the desired value. Pressures up to approximately 7,000 lb/in.^{2} were obtained by initially surrounding the pressure vessel with dry ice, thus liquefying the CO_2 in the vessel and producing higher pressures on heating. Still higher pressures were achieved with a motor-driven hydraulic pump which forced oil upward against a piston acting as a separator in a vertical pressure cylinder, the volume above the separator having been filled initially with CO_2 at tank pressure.

Medical-grade CO_2 was used, and in runs up to 1,000 lb/in.^{2} it was held before use in a pressure cylinder containing magnesium perchlorate, to remove any traces of water. A number of duplicate runs were made without this procedure, and the results obtained were the same. The CO_2 was therefore used at higher pressures with no further treatment. All pressures were read directly from Bourdon-type gauges. The temperature was continually recorded on a strip-chart instrument, using calibrated chromel-alumel thermocouples.

Upon completion of a run, the furnace was immediately pulled back from the pressure vessel and the vessel cooled by an air blast. All samples were examined by means of powder X-ray diffraction, as described in the following paper (Goldsmith, Graf, and Joensuu, 1955).

The Equilibrium Thermal Decomposition Curve of Dolomite

The P_{CO_2}, T curve of dolomite is shown in Fig. 1, plotted as log P_{CO_2} vs. $1/T_{°K}$. A portion of this curve is replotted in Fig. 2 with P_{CO_2} and T as co-ordinates. The points that define the curve are included in the thermal data of Table 1, and were determined by runs made with dolomite from Serra das Eguas, Brazil. This dolomite occurs as large water-clear crystals, contains less than 0·5 mol per cent Fe and Mn carbonate, and has a Ca : Mg ratio of 1 : 1 within the limits of error of wet-chemical and spectrographic analyses. As a further test of the Ca : Mg ratio, powder X-ray diagrams of the Serra das Equas material and several other synthetic and natural dolomites, essentially free of iron and manganese, were compared. The spacings of several sensitive back-reflections were the same within the limits of error of measurement.

Total decomposition of the dolomite does not take place at pressures and temperatures near the equilibrium curve, within the times used for these experiments. However, even a slight amount of decomposition is detectable by the appearance of the strongest reflections of periclase and calcite. At the higher temperatures and pressures, observable decomposition takes place in a few hours, and the position of the curve can be readily ascertained within a few degrees. At pressures below about 100 lb/in.^{2}, the reaction proceeds quite slowly, and runs of several weeks were necessary. Even so, under these conditions there is some doubt as to the stability of the dolomite in those runs in which decomposition was not detectable. The lower portion of the curve may be biased toward higher temperatures and is therefore indicated as a dashed line in Fig. 1.

The use of a log P vs. $1/T_{°K}$ plot, which for an ideal system should produce a straight line, increases the reliability of the extrapolation of the data. The dashed

Table 1

Runs using Brazilian dolomite as starting material (see Table 4 also). The runs labelled 14·7 lb/in.^{2} CO_2 were maintained approximately at this pressure by periodic bleeding of the system. The runs labelled "air" were carried out in open vessels, and the effective CO_2 pressure must have varied somewhat with the partial pressure of CO_2 in the immediate environment.

C, P, and D refer to the presence, as observed in X-ray diffraction diagrams, of calcite, periclase, and dolomite, with no consideration of solid solution. Parentheses indicate quantities near the limit of detection.

P_{CO_2} *in lb/in.*^{2}	T°C	*Time (hrs)*	*Products*
20,000	863	1·5	C + P + D
20,000	852	1·5	D
20,000	841	1·5	D
20,000	831	1·5	D
10,000	796	5	C + P + D
10,000	788	5	D
10,000	780	4·5	D
10,000	763	5	D
8,000	803	5	C + P + D
3,600	740	4	C + P + D
3,600	725	4	C + P + D
3,600	709	4	D
975	680	44	C + P + D
900	642	44	C + (P) + D
900	633	24	D
860	636	41	(C) + (P) + D
400	630	6	(C) + (P) + D
400	619	41	C + P + D
400	615	52	C + P + D
400	611	13	D
400	611	45	(C)* + D
400	605	52	(C)* + D
400	600	40	D
250	600	44	C + P + D
250	598	40	(C)* + D
250	596	46	D
250	590	14	D
250	561	47	D
240	582	54	D
240	563	62	D
115	555	96	D
115	550	87	D
115	550	192	D
100	563	110	C + (P) + D
100	555	91	D
100	553	96	D
40	495	162	D
14·7	508	408	(C)* + D
14·7	502	381	D
14·7	493	329	D
14·7	484	340	D
(air)	416	46	D
(air)	405	816	C + P + D
(air)	386	165	D
(air)	380	768	C* + D
(air)	362	840	(C)* + D
(air)	345	1,630	D

* Periclase was not observed in the diffraction diagram, but its presence may be inferred from the development of calcite.

upper portion of the curve represents an extrapolation to 50,000 lb/in.^{2} at 975°C, a region not attainable with the pressure vessels on hand.

As a check on the validity of the curve, dolomite was produced by synthesis in its stability field. For any run in which no decomposition of dolomite can be observed, the synthesis of dolomite eliminates doubt as to the stability relations.

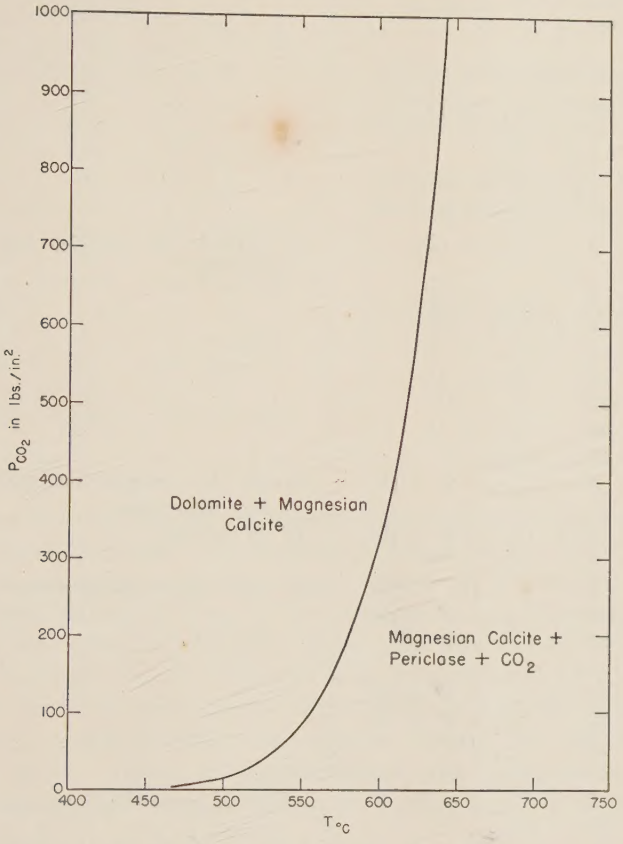

Fig. 2. Equilibrium thermal decomposition curve of dolomite at moderate CO_2 pressures, replotted from Fig. 1.

The starting material for this solid-state synthesis was a calcareous algal material from Bermuda, containing approximately 20 mol per cent $MgCO_3$ in solid solution. A material of this sort was considered to be the most desirable for solid-state reaction; only cation migration over very short distances in the disordered solid solution is required to produce dolomite with an ordered Ca—Mg configuration. This reaction should proceed more readily than one requiring reorganization of two phases, such as calcite and magnesite. At temperatures and pressures at which dolomite is unstable, the algal material breaks down to periclase and a calcite phase. The data for the runs using algal material are presented in Table 2. Fig. 3 contains the curve of Fig. 1, with algal runs plotted. The runs substantiate the data from which Fig. 1 was derived, and the curve therefore represents an equilibrium reaction determined from both directions.

Table 2

Runs made using algal magnesian calcite as starting material. C, P, D, and M refer to the presence, as observed in X-ray diffraction diagrams, of calcite, periclase, dolomite, and magnesite. Parentheses indicate quantities near the limit of detection, and numerical subscripts give the mol per cent Mg substitution in the calcites.

P_{CO_2} *in lb/in.*^{2}	T°C	*Time (hr)*	*Products*	*Remarks*
21,000	704	46	$C_{14\cdot0}$ + D	
20,000	863	1·5	$C_{21\cdot1}$	
20,000	841	1·5	$C_{21\cdot6}$	
20,000	831	1·5	$C_{21\cdot3}$	
12,000	854	27	$C_{6\cdot0}$ + P	
10,000	796	5	$C_{21\cdot1}$ + (D)	"D" formed on cooling, has diffuse X-ray reflections
10,000	788	5	$C_{20\cdot5}$ + (D)	
10,000	780	4·5	$C_{19\cdot7}$ + D	
10,000	762	4	$C_{18\cdot8}$ + D	
10,000	697	26	$C_{13\cdot5}$ + D	
9,700	548	122	$C_{7\cdot2}$ + D	
8,500	650	96	$C_{11\cdot6}$ + D	
8,000	853	24	$C_{4\cdot1}$ + P	
8,000	803	5	$C_{9\cdot2}$ + P + (D)	Ca-rich "D," formed on cooling, has diffuse X-ray reflections
5,000	801	5	$C_{3\cdot7}$ + P + (D)	"D" is Ca-rich
3,600	734	4	$C_{16\cdot7}$ + D	
3,600	725	4	C + (P) + (D)	"D" has diffuse X-ray reflections
3,050	725	840	$C_{5\cdot3}$ + P + (M)	
3,000	807	24	$C_{1\cdot6}$ + P	
2,000	752	44	$C_{2\cdot9}$ + P	
990	750	23	$C_{1\cdot4}$ + P + (D)	
990	700	23	$C_{3\cdot1}$ + P + (D)	
975	680	44	$C_{3\cdot1}$ + P	
975	650	44	$C_{11\cdot1}$ + D	
820	619	3	$C_{(11\cdot4)}$ + D	Diffuse X-ray reflections, not in equilibrium
750	644	44	$C_{4\cdot0}$ + P	
750	634	40	C + P + D	
750	630	47	C + P + D	
525	575	840	$C_{8\cdot1}$ + D	
500	802	93	$C_{0\cdot7}$ + P	
500	698	118	$C_{1\cdot5}$ + P	
450	619	46	$C_{4\cdot5}$ + P + (D)	"D" has diffuse X-ray reflections
410	605	52	$C_{9\cdot0}$ + D	
285	800	65	C_0 + P	
285	700	65	$C_{1\cdot1}$ + P	
240	588	54	C + (P) + D	
220	589	44	C + P + D	Diffuse X-ray reflections; not in equilibrium
220	571	14	$C_{9\cdot7}$ + D	Diffuse X-ray reflections; not in equilibrium
220	546	42	$C_{8\cdot6}$ + D	Diffuse X-ray reflections; not in equilibrium
115	557	96	C + P + D	
115	552	87	No reaction	
115	552	192	No reaction	

Table 2—continued

P_{CO_2} *in* $lb/in.^2$	$T°C$	*Time* (*hr*)	*Products*	*Remarks*
115	525	190	C + D	
100	557	91	C + P + D	
40	515	165	C + D	Diffuse X-ray reflections; not in equilibrium
40	495	162	$C_{a \rightarrow 50}$	Wide range of metastable Mg-calcites
14·7	522	528	$C_{2\cdot2}$ + P	Diffuse X-ray reflections; not in equilibrium
14·7	508	408	No reaction	
14·7	505	381	$C_a + C_b$ + P	Two Mg-calcites; not in equilibrium
14·7	499	528	C + P	Diffuse X-ray reflections; not in equilibrium
14·7	494	329	No reaction	
14·7	484	340	No reaction	
(air)	426	120	No reaction	
(air)	405	816	$C_a + C_b$	Two Mg-calcites; not in equilibrium
(air)	402	174	No reaction	
(air)	361	840	No reaction	
(air)	350	768	C + D	
(air)	345	1,630	No reaction	

In a narrow zone at the curve, many of the algal runs yielded small amounts of both dolomite and periclase. These results, which do not affect the validity of the curve, could be a consequence of several factors: (1) Dolomite may be produced in its stability field during heating of the sample before bleeding off of extraneous pressure, and may then not be fully decomposed during the run in which MgO is formed as a stable phase, (2) Dolomite may be produced by back-reaction during cooling, under pressure, through the dolomite stability field (this point is discussed below), (3) Slight temperature fluctuations during the run may produce both dolomite and MgO. Again, at temperatures and pressures near the curve, the tendency to destroy an unstable phase is minimized, (4) There may be a slight temperature gradient in the pressure vessel.

The Dolomite Decomposition Reaction and the Stability of Magnesian Calcites

Early in the process of investigating the equilibrium curve it was observed that the calcites produced had X-ray spacings indicative of Mg in solid solution, and that the amount of Mg increased with temperature and CO_2 pressure. The amount of Mg in solid solution in the calcite is also strongly dependent upon whether P,T conditions fall in or out of the dolomite stability field, i.e., whether the calcite is in equilibrium with dolomite, or with periclase and CO_2. These considerations are discussed below, but first it is necessary to clarify the reactions which take place.

The thermal decomposition of dolomite is generally expressed by the reaction:

$$\underset{\text{DOLOMITE}}{CaMg(CO_3)_2} \rightleftharpoons \underset{\text{CALCITE}}{CaCO_3} + \underset{\text{PERICLASE}}{MgO} + CO_2 \qquad (1)$$

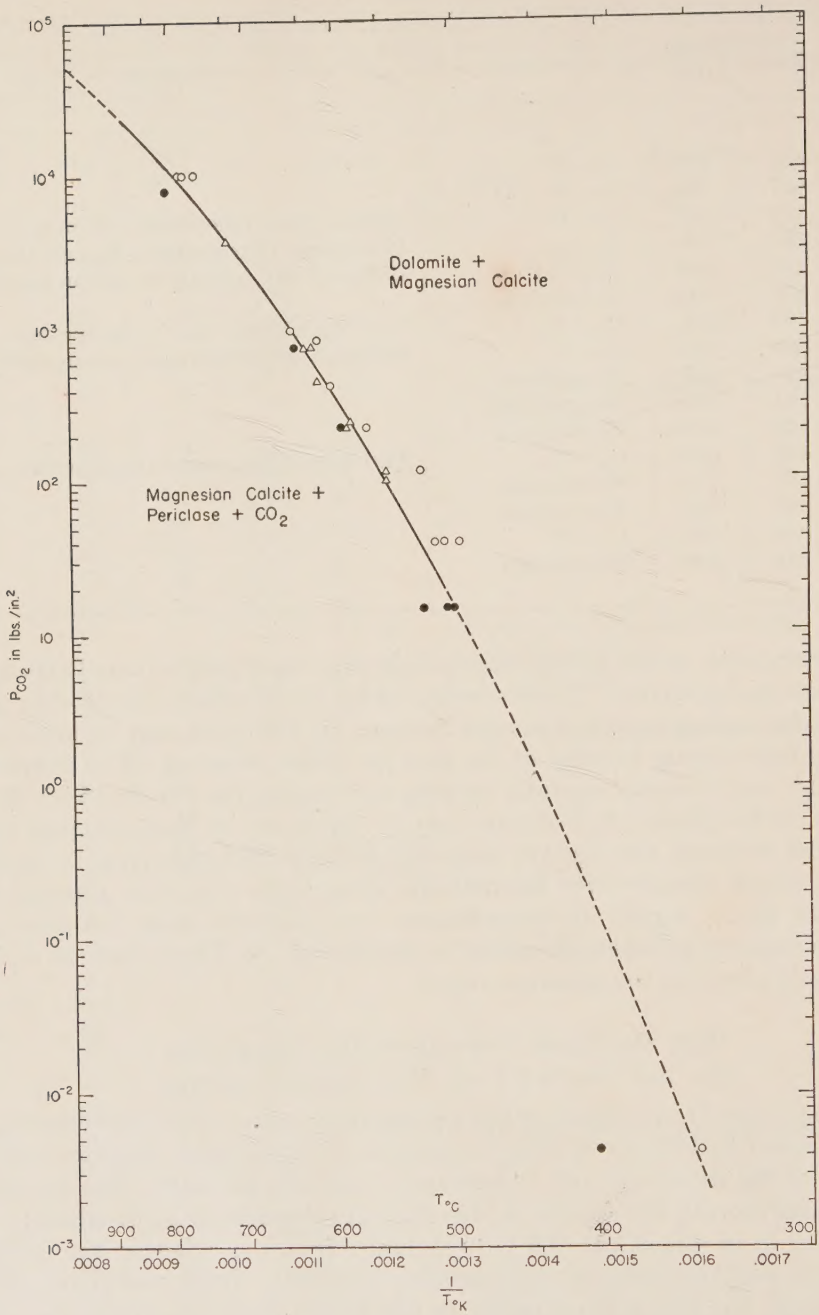

Fig. 3. The curve of Fig. 1 replotted. The points represent the results of runs using magnesian calcite as starting material. Open circles—dolomite formed from algal material; filled circles—MgO formed from algal material; triangles—both dolomite and MgO formed.

The variable Mg substitution in the calcite is not taken into account in this equation, and a more rigorous expression applicable to the curve (Figs. 1–3) is:

$$\underset{\text{DOLOMITE}}{Ca_1Mg_1(CO_3)_2} \rightleftharpoons \underset{\text{MAGNESIAN CALCITE}}{Ca_1Mg_{(1-x)}(CO_3)_{(2-x)}} + \underset{\text{PERICLASE}}{xMgO} + xCO_2 \qquad (2)$$

The synthesis of dolomite from the algal magnesian calcite can be expressed by the following equation, rewriting the above expression for magnesian calcite to simplify description of the reaction products:

$$\underset{\text{MAGNESIAN CALCITE I}}{Ca_1Mg_x(CO_3)_{(1+x)}} \rightleftharpoons \underset{\text{DOLOMITE}}{Ca_yMg_y(CO_3)_{2y}} + \underset{\text{MAGNESIAN CALCITE II}}{Ca_{(1-y)}Mg_{(x-y)}(CO_3)_{(1+x-2y)}} \qquad (3)$$

where $x < 1$ and magnesian calcite II is poorer in Mg than magnesian calcite I, i.e., $y < x$.

The remaining expression is concerned with the decomposition of magnesian calcite at temperatures and CO_2 pressures under which dolomite is not stable:

$$\underset{\text{MAGNESIAN CALCITE I}}{Ca_1Mg_x(CO_3)_{(1+x)}} \rightleftharpoons \underset{\text{MAGNESIAN CALCITE II}}{CaMg_{(x-y)}(CO_3)_{(1+x-y)}} + \underset{\text{PERICLASE}}{yMgO} + yCO_2 \qquad (4)$$

where $y \gtrless x$, i.e., magnesian calcite II is poorer in Mg than magnesian calcite I.

The equilibrium between dolomite and magnesian calcite

The magnesian calcite algal material used was precipitated by organisms and contains a high magnesium concentration that, as will become evident, is metastable under standard conditions. It would be expected that equilibrium according to equation (3) would be reached most readily with this reactive material. This reaction does proceed readily at all temperatures down to about 500°C. Above this temperature, dolomite and well-crystallized magnesian calcite are produced in a reasonable time, but reorganization is exceedingly slow at lower temperatures. When equilibrium is established, all X-ray reflections are sharply defined, and the $K\alpha_1$-α_2 doublets are well resolved, using Fe radiation, in the back-reflection region. This is in marked contrast to the original state of crystallization of the algal material, the X-ray diagrams of which show reflections to be diffuse and back reflections virtually absent (Fig. 9, c and d).

The equilibrium, as illustrated by equation (3), is concerned only with carbonate phases. Inasmuch as CO_2 and MgO are not involved, the reaction is insensitive to CO_2 pressure* and MgO concentration, and is influenced only by temperature.

Table 3 presents data on those runs in Table 2, made with the algal material in the stability field of dolomite, in which equilibrium was reached. The relative reflection intensities from the co-existing dolomite and magnesian calcite can also be used as an indication of the amount of Mg in the calcite phase, but this method is far less sensitive than the X-ray spacing measurements and was not used.

* The effect of total pressure on this and other reactions in this system is not evaluated.

Table 3

Runs made with algal material in the stability field of dolomite and used for plotting Fig. 4. At the higher temperatures, the data may be slightly biased in the direction of high Mg content. This point is discussed further in connection with the composition versus cell-size curves presented by Goldsmith, Graf, and Joensuu (1955).

T°C	*Mol per cent* $MgCO_3$	*Time (hr)*	P_{CO_2} *lb/in.*^{2}
796	21·1	5	10,000
788	20·5	5	10,000
780	19·7	4·5	10,000
762	18·8	5	10,000
734	16·7	4	3,600
704	14·0	46	21,000
697	13·5	26	10,000
650	11·6	96	8,500
650	11·1	44	975
605	9·0	52	410
575	8·1	840	525
548	7·2	122	9,700

The runs from Table 3 are plotted as Fig. 4. This figure is the unmixing curve, from 500° to 800°, between calcite and dolomite. Above approximately 800°C all the Mg in the original magnesian calcite algal material is retained in solid solution

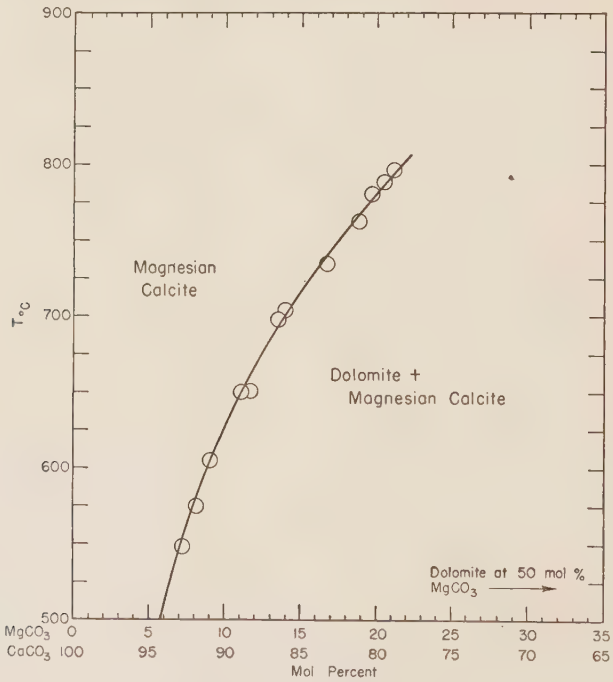

Fig. 4. A portion of the exsolution curve in the system $CaCO_3$—$MgCO_3$, determined at CO_2 pressures sufficient to prevent decomposition. See legend of Table 3.

with none left for the formation of dolomite. Thus the material becomes useless for investigation of the equilibrium at higher temperatures.

In Fig. 5, the vertical lines in the dolomite stability field are derived from Fig. 4 and indicate the amount of Mg stable in calcites that are in equilibrium with dolomite. The lines are vertical because, as stated earlier, CO_2 pressure does not affect the equilibrium in this field.

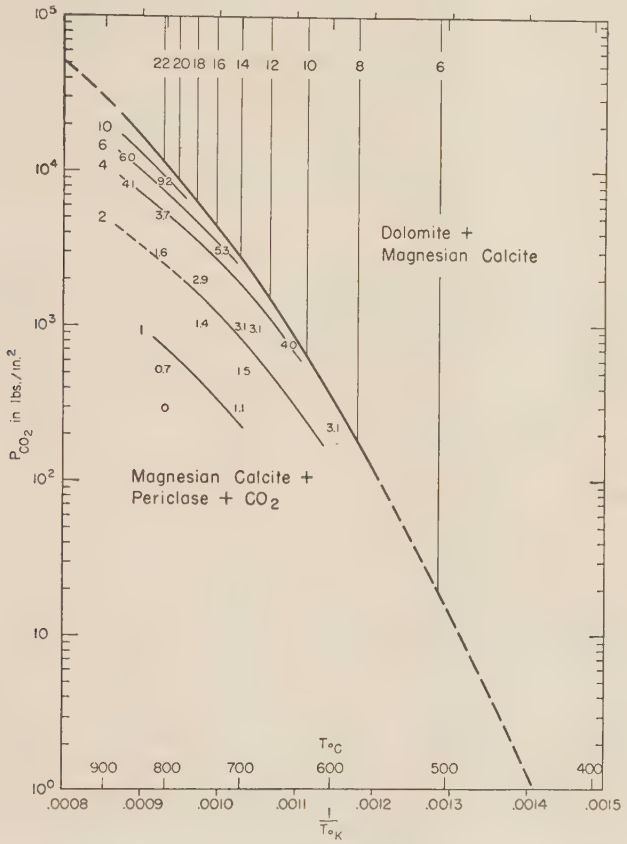

Fig. 5. The equilibrium thermal decomposition curve of dolomite shown in Fig. 1, together with lines of equal Mg concentration (mol per cent) in the magnesian calcites. Mg concentrations of the calcites in equilibrium with dolomite are independent of P_{CO_2}, resulting in vertical iso-Mg lines. The numbers give the Mg concentration (mol per cent) of calcites in equilibrium with MgO. Algal magnesian calcite was used as starting material for these runs.

The equilibrium between periclase and magnesian calcite

Reaction (4) illustrates the relations in the field to the left of the dolomite equilibrium curve (Figs. 1 and 3), where dolomite is not stable. It is apparent that under these conditions the reaction is influenced by the CO_2 pressure as well as by the temperature.

In Fig. 5, based upon runs made with the algal material, the numbers to the left of the curve represent the magnesium substitution in the calcites, expressed as mole per cent. These data, which are also included in Table 2, are consistent

enough among themselves so that it is possible to draw a number of iso-Mg lines. These lines, if extended, must join the vertical iso-Mg lines of the dolomite stability field. The iso-Mg lines in the field of dolomite decomposition may be looked upon as a series of curves, each representing the stability limit of a particular magnesian calcite, as expressed by reaction (4). Thus an infinite family of curves expressing the stability of the magnesian calcites branches out from the P,T curve of dolomite. It is apparent both from inspection of reaction (4) and from the data of Fig. 5 that the Mg substitution in the calcites is increased by increase in CO_2 pressure, at any particular temperature. Increasing the temperature at any particular CO_2 pressure progressively decreases the stability of the Mg^{++}—$O^{=}$ bonds in the carbonate, resulting in the exsolution of Mg as MgO, whereas the Ca^{++}—$O^{=}$ bonds are not weakened to the point where $CaCO_3$ decomposes. This relation is shown by the increasing temperature of decomposition in the series magnesite—dolomite—magnesian calcites—calcite.

Table 4

Runs made in the decomposition field with dolomite as a starting material. C, P, and M refer to calcite, periclase, and magnesite. Numerical subscripts give the mol per cent Mg substitution in the calcites. Parentheses indicate quantities near the limit of detection.

P_{CO_2} *in lb/in.*^{2}	T°C	*Time (hr)*	*Products*
12,000	854	27	$C_{6.7}$ + P + (M)
8,000	853	24	$C_{3.1}$ + P
5,000	801	5	$C_{13.5}$ + P
3,050	725	840	$C_{6.2}$ + P
3,000	807	24	$C_{4.3}$ + P
2,000	752	44	$C_{6.4}$ + P
990	750	23	$C_{4.2}$ + P
990	700	23	$C_{6.4}$ + P
500	802	93	C_0 + P
500	698	118	$C_{6.9}$ + P + (M)
285	800	65	$C_{0.8}$ + P
285	700	65	$C_{1.6}$ + P
200	800	21	C_0 + P

Increase in temperature at any particular CO_2 pressure increases the entropy of the carbonate, a condition that would normally permit more Mg to become stable in the solid solution. In the present case, however, the decomposition relations not only prevent additional Mg from being taken into solid solution when the temperature is increased, but actually result in the loss of some of the Mg already in the structure.

The data for the decomposition runs made with dolomite as a starting material have been collected in Table 4. The calcite formed from the decomposition of dolomite should have the same Mg concentration as that formed from the algal material at the same T and P_{CO_2}.*

* The only difference in the two cases lies in the quantity of MgO in the system. Inasmuch as periclase is stable in this field, the absolute amount of MgO, aside from that necessary for the magnesian calcite, will only be expressed in the formation of more or less periclase, which exists here as a separate phase.

The data of Table 4 cannot, however, be used in the same fashion as were the algal points in Fig. 5. The values of Mg content of these calcites are for the most part higher than those derived from the algae, and in addition show an uncertainty among themselves.

It is quite difficult to attain equilibrium when dolomite is used as a starting material. The decomposition is a rather slow process, and it has already been mentioned that at temperatures and pressures near the equilibrium curve, complete decomposition is usually not obtained, even in long runs. The inconsistent results mentioned above are an expression of this difficulty. The X-ray patterns of the decomposition products of dolomite show periclase reflections that are quite sharp, but all the magnesian calcite reflections are diffuse. This is in marked contrast to the patterns of calcite produced from the algal material (Fig. 9, e and f).

Additional observations

A number of runs on different starting materials were made to check the data obtained from the algal magnesian calcite and the dolomite. Co-precipitated calcium and magnesium carbonates were obtained by pouring together solutions of K_2CO_3, $CaCl_2$, and $MgCl_2$ of various initial concentrations. The precipitates were washed by decantation until the chloride content was reduced to a low value, then dried. The products were very finely divided and gave poor diffraction patterns. Two of the precipitated carbonates were used for the experimental work, and the compositions were determined by spectrographic analysis:

	Mol per cent $CaCO_3$	Mol per cent $MgCO_3$
No. 1	54	46
No. 2	86	14

The data on runs made with these materials are listed in Table 5. On the whole they check quite well with the data already presented. The equilibrium products formed during the runs made with the precipitates proved to be highly reactive, however, and in most cases a back reaction during cooling of the pressure vessel was observed to have taken place. This phenomenon was but rarely observed in runs with the algal material or dolomite, and may be a consequence of the small amount of chloride impurity.

In experiments 3, 13, 14, and 15 (Table 5), magnesite was observed as one of the products. Periclase was also present, and it is evident that the magnesite was produced by reaction of MgO and CO_2 during cooling through the stability field of magnesite. The X-ray reflections of the magnesite are rather diffuse, indicative of small crystal size or crystal imperfection, a consequence of the rapid crystallization. In runs 8 and 11, back reaction during cooling through the stability field of dolomite produced a complete series of metastable magnesian calcites ranging in composition from a magnesian calcite, stable under the conditions of the run, all the way to dolomite. The X-ray powder patterns of the runs that illustrate this phenomenon have "bands" adjacent to the lines of the magnesian calcite. These "bands" end abruptly at the spacings characteristic of dolomite. This effect is illustrated in Fig. 9g. The intermediate materials that produce the band reflections represent all stages in the formation of dolomite, i.e., all stages in the incorporation

Table 5

Additional runs, using co-precipitated Ca-Mg carbonates, as well as mixtures of calcite and magnesite, as starting materials. Subscripts on the precipitate designations refer to mole percentages of $CaCO_3$ and $MgCO_3$. Numerical subscripts on the product designations represent mol per cent Mg substitution in the calcites. C, D, P, and M refer to calcite, dolomite, periclase, and magnesite. Parentheses indicate quantities near the limit of detection.

Run No.	*Starting material*	P_{CO_2} *in lb/in.*^{2}	T°C	*Time (hr)*	*Products*	*Remarks*
1	$Ca_{86}Mg_{14}$ ppt.	920	750	18	$C_{1\cdot2}$ + P	
2	do.	975	700	25	$C_{2\cdot2}$ + P	
3	do.	975	650	25	$C_{5\cdot1}$ + P + (M)	
4	do.	920	625	18	C + D + P	
5	$Ca_{54}Mg_{46}$ ppt.	8,000	853	24	C + D + P	Range of metastable phases near D in compn., produced by back reaction
6	do.	20,000	852	1·5	(C) + D	D contains ~1 mol% excess $CaCO_3$
7	do.	20,000	841	1·5	(C) + D	D contains ~1·6 mol % excess $CaCO_3$
8	do.	3,000	807	24	$C_{2\cdot1-50}$ + P	
9	do.	8,000	803	5	C + D + P	See remarks for No. 5
10	do.	5,000	801	5	C + D + P	See remarks for No. 5
11	do.	2,000	752	44	$C_{2\cdot6-50}$ + P	
12	do.	920	750	18	$C_{1\cdot0}$ + P	
13	do.	975	700	25	$C_{2\cdot0}$ + P + (M)	
14	do.	975	650	25	$C_{4\cdot6}$ + P + M	
15	do.	920	625	18	C + D + P + M	See remarks for No. 5
16	75 wt. % calcite + 25 wt. % magnesite	21,000	704	46	C + D + M	X-ray reflections of C diffuse; spottiness of M reflections indicates M is unreacted starting material
17	do.	12,000	854	27	$C_{6\cdot2}$ + P	

of Mg into the magnesian calcite by reaction with MgO and CO_2.* In runs 5, 9, and 10, dolomite was produced by back reaction, and although line broadening shows it to be associated with some variable magnesian calcite near dolomite in composition, the whole range is not shown.

These data give some indication of how rapidly reactions can take place in the system under certain conditions. This is in contrast to the sluggish behaviour of the products from dolomite itself, as discussed above. Once thermally decomposed, however, dolomite can be resynthesized. A sample of natural dolomite was held at

* When X-ray patterns of this type are prepared without rotating the sample, all reflections other than the bands are spotty, clearly differentiating the more coarsely crystalline equilibrium products from the fine-grained back reaction products.

800°C and 200 lb/in.^{2} for twenty-one hours. The decomposition products, a nearly pure calcite and finely divided MgO, were then held at 704°C and a CO_2 pressure of 21,000 lb/in.^{2} for forty-six hours. At the end of this time it was observed that approximately 90 per cent reaction back to dolomite had taken place.

Several runs were also made with mechanical mixtures of finely divided calcite and synthetic magnesite. Two runs, with mixtures of 75 wt. per cent $CaCO_3$ and 25 wt. per cent $MgCO_3$, one in the stability field, of dolomite and the other in the decomposition field, are listed (Nos. 16 and 17), in Table 5. Run No. 16 had not reached equilibrium in forty-six hours, as some unreacted magnesite was still present. This contrasts with runs using algal material, where equilibrium is established in considerably less time under the same P_{CO_2}, T conditions. Run No. 17 reached equilibrium, and the Mg content of the calcite checks well with that determined from algal material.

The Nature of the P_{CO_2}, T Curve

The equilibrium thermal decomposition curve of dolomite (Figs. 1–3) represents a true univariant equilibrium. Although the calcite phase in reaction (2) varies in composition with P_{CO_2} and T, the phase rule is strictly applicable inasmuch as the composition of phases does not enter into the expression $P + F = C + 2$. The fact that dolomite is in equilibrium not with a pure calcite, but with a variable solid solution, does not negate the univariant nature of the reaction. This fact, as explained below, does, however, complicate the extraction of thermochemical data from the curve.

The plot of log P_{CO_2} vs. $1/T_{°K}$ is not a straight line, as would be the case in an ideal system. The curvature may be a consequence of several factors, such as the above-mentioned variation in composition of the magnesian calcites and the non-ideal behaviour of CO_2 gas. The computation of ΔH values for different pressures and temperatures can be made with appropriate thermodynamic expressions, using Kennedy's data (1954) for CO_2 with a suitable ΔV correction for the CO_2 tied up in the magnesian calcite. The simple Clausius-Clapeyron equation ($dP/dT = \Delta H/T\Delta V$) cannot, however, be used, because the ΔH term for every point on the curve contains a contribution from the magnesian calcite in equilibrium at that point, and this variable contribution involves unknown values of the heats of mixing of the magnesian calcites. It would appear that, at the present state of knowledge, no fundamental significance could be attached to ΔH values obtained from this curve.

The Nature of the Dolomites Produced

The dolomite structure is an ordered calcite structure in which half the calcium positions are occupied by magnesium; cation planes are alternately occupied by calcium and by magnesium (Wasastjerna, 1924; Wyckoff and Merwin, 1924). By contrast, the magnesian calcites have variable magnesium concentration, and the ordering of Ca and Mg just described is not encountered. The principal superstructure reflections observed in dolomite, indicative of Ca-Mg ordering, are (100), (221), and (11$\bar{1}$), indexed on the basis of the true rhombohedral unit cell (Bradley, Burst, and Graf, 1953). In all runs in which equilibrium had been

reached, and in which a sufficient amount of dolomite was present so that the relatively weak superstructure reflections would be intense enough to register, these reflections are visible. In several runs that did not reach equilibrium, a phase was obtained that had spacings equivalent to, or near, those of dolomite but with somewhat diffuse reflections. The ordering reflections in such cases were weak or absent. An example is run No. 10, Table 5, where the "neodolomite" was formed rapidly as a reaction product during cooling. Nevertheless it is evident that at the relatively high temperatures of this investigation, the ordering required to form dolomite proceeds readily.

The measured X-ray spacings of dolomites in equilibrium with the magnesian calcites (Fig. 4) show the dolomites to be very close to the theoretical composition. In the X-ray diagrams for a number of the lower-temperature runs in the field of dolomite, the strongest reflection, (112), of a substance approaching dolomite in composition but with up to approximately 10 mol per cent excess Ca as evidenced by the (112) spacing, was observed. Equilibrium had not been reached, for a considerably greater amount of "dolomite" should have been present than was observed in the final product. This "dolomite" was not abundant enough to determine whether or not superstructure lines were present.

It would appear, however, that at least at the higher temperatures, a slight but real excess of Ca is present in the dolomites in equilibrium with magnesian calcites. This can be observed in some X-ray patterns which show superstructure reflections, as a slight shift in X-ray spacings; at 800°C the deviation is of the order of 1–1½ mol per cent.* In most runs the percentage of dolomite formed was insufficient to produce either superstructure reflections or reliable back-reflection measurements. In these cases the measurable (112) reflection showed deviations indicating up to ~5 mol per cent excess $CaCO_3$ at ~800°C. The amount of deviation from the 1 : 1 Ca : Mg ratio that can be tolerated by the dolomite structure without loss of the ordering reflections is not known.

Consideration of the System $CaCO_3$—$MgCO_3$ at Higher Temperatures and Pressures

Although no experimental work above approximately 860°C and 20,000 lb/in.² has been done, it is of interest to speculate as to conditions at higher temperatures and pressures. $CaCO_3$ is reported to melt at 1,339°C under ~15,000 lb/in.² CO_2 (Smyth and Adams, 1923), to a eutectic of 0·38 wt. per cent CaO in $CaCO_3$. The melting relations of the system as a whole are, however, unknown.

A necessarily crude extrapolation of the unmixing curve of Fig. 4 indicates that a magnesian calcite of the composition of dolomite might become stable at about 1,000°C. Extrapolation of the equilibrium curve (Figs. 1–3) indicates that at this temperature the CO_2 pressure required to prevent decomposition is about 58,000 lb/in.². If it is assumed that this extrapolation is justified in principle, and that melting phenomena do not intervene, then a diagram of the type shown by Fig. 6 would be applicable. The top of the curve in this case represents disordering of the

* This measurement was made using the slope of the composition vs. X-ray spacing curve of Fig. 1 in the following paper (Goldsmith, Graf, and Joensuu, 1955). The error introduced in measuring the composition of a dolomite rather than a magnesian calcite by this method was greatly reduced by using the Brazilian dolomite as the measuring standard.

Figs. 6–8. Hypothetical subsolidus relations between $CaCO_3$ and dolomite. Possible complications due to melting are ignored.

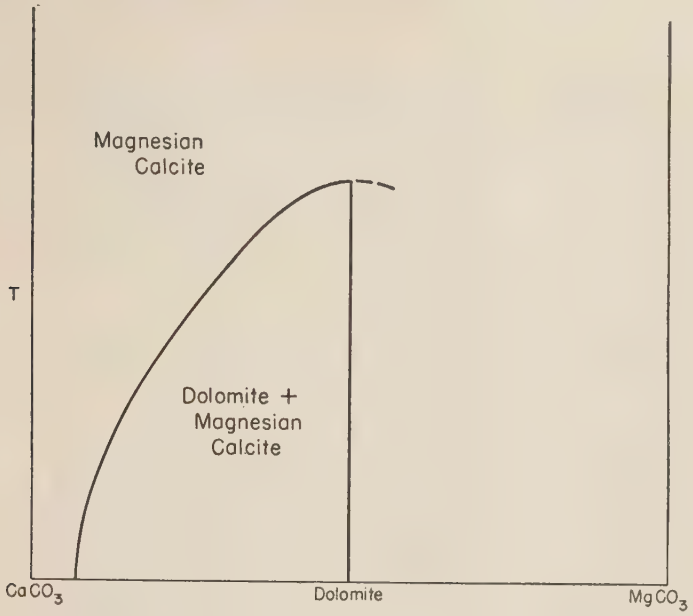

Fig. 6

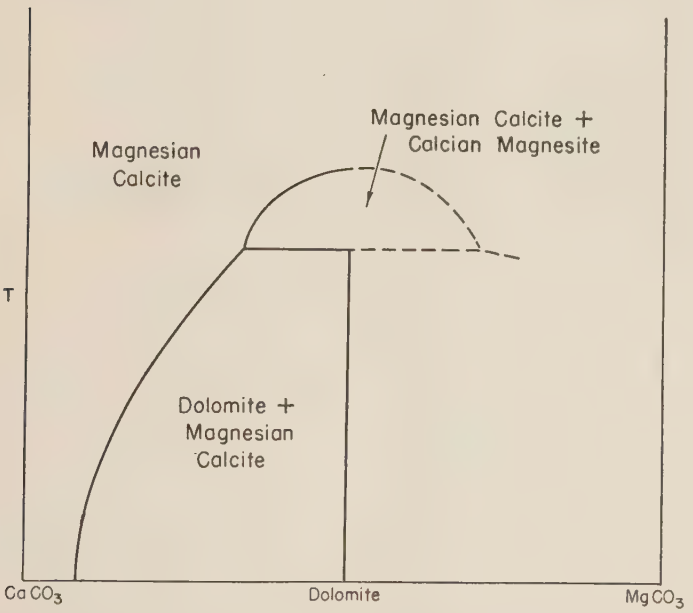

Fig. 7

dolomite; the figure is drawn as if dolomite retains the 1 : 1 Ca : Mg ratio up to the hypothetical disordering temperature.

Fig. 7 illustrates another possibility, in which at some temperature dolomite becomes unstable, breaking down into a magnesian calcite and a calcian magnesite. Again possible complications due to melting have been neglected.

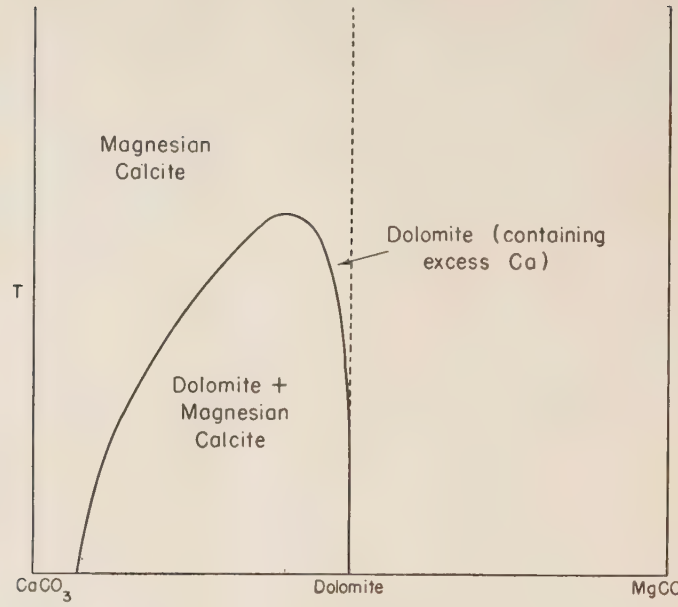

Fig. 8a

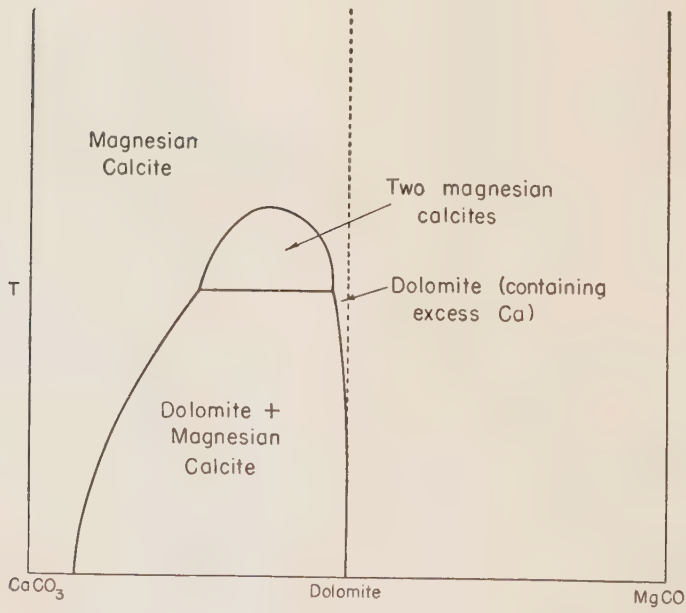

Fig. 8b

Figs. 8a and 8b illustrate more realistic cases, in view of the experimental results, in which dolomite takes up a small excess of Ca at higher temperatures. In Fig. 8a magnesian calcite is shown in equilibrium with dolomite; according to this diagram the dolomite must transform to a disordered magnesian calcite at

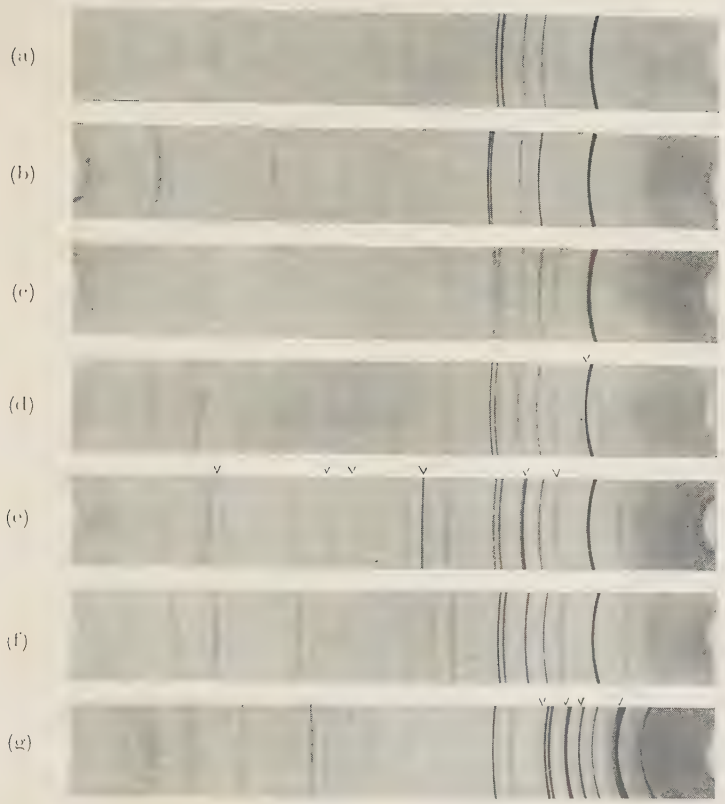

Fig. 9. Selected X-ray diffraction diagrams.
Diagrams (a) to (f), Fe radiation, Mn filter; (g) Cu radiation, Ni filter.

(a) Specpure calcite (Johnson, Matthey and Company).
(b) Dolomite, Serra das Eguas, Brazil.
(c) Calcareous algae, ~20 mol per cent $MgCO_3$, Bermuda. Note diffuseness of pattern, high background, and virtual absence of back reflections.
(d) Bermuda calcareous algae run at 697°C and 10,000 lb/in.^{2} CO_2 for twenty-six hours, in the stability field of dolomite. Note the sharpness of the reflections of the newly formed magnesian calcite phase as compared with (c). The principal dolomite reflection is indicated by an arrow.
(e) Brazilian dolomite run at 807°C and 3,000 lb/in.^{2} CO_2 for twenty-four hours. The calcite reflections are rather diffuse; the MgO reflections, indicated by arrows, are sharp.
(f) Bermuda calcareous algae run at 698°C and 500 lb/in.^{2} CO_2 for forty-eight hours. All reflections are sharp in contrast to (e).
(g) Precipitated Ca-Mg carbonate No. 1 (46 mol per cent $MgCO_3$), run for twenty-four hours at 807°C and 3,000 lb.in.^{2} CO_2. Arrows indicate bands adjacent to strongest calcite reflections, representing a compositional range all the way to dolomite.

some unspecified composition or range of compositions along the upper portion of the right limb of the exsolution curve. In Fig. 8b, the horizontal line indicates a temperature at which a specific amount of excess Ca in the dolomite, in equilibrium with magnesian calcite, induces a disordering of the dolomite, resulting in an equilibrium between two magnesian calcites.

Relations in the region between 50 and 100 mol per cent $MgCO_3$ have not been indicated in these hypothetical diagrams. Although no experimental work has been carried out on this portion of the system, it might be expected that less Ca would be substituted in $MgCO_3$ than Mg in $CaCO_3$. The difference in ionic size of Ca^{++} and Mg^{++} is considerable (1·06 Å vs. 0·78 Å, Goldschmidt values), and extensive substitution of the larger atom for the smaller one should be less likely than the reverse.

Petrologic Interpretations

The experimental results have particular application to carbonates from metamorphic environments. The equilibrium thermal decomposition curve sets an *upper* temperature limit, at any specific CO_2 pressure, for the existence of dolomite in dolomite or calcite-dolomite rocks.* If the CO_2 produced by the decomposition reaction in this system is able to escape, decomposition of dolomite can take place at a temperature in the neighbourhood of 375°C.

Thermal metamorphism of a Ca-Mg carbonate rock should, if sufficient CO_2 pressure is maintained, develop dolomite in equilibrium with magnesian calcite, as illustrated by Fig. 4. Many metamorphic carbonates, more fully described by Goldsmith, Graf, and Joensuu (1955), do show the association of dolomite with a calcite containing a sufficient amount of magnesium to indicate that rather high temperatures had been attained. Furthermore, one might expect that exsolution features might have developed during the cooling of a magnesian calcite stable at elevated temperatures (see Fig. 4). Evidence for this phenomenon is presented by Goldsmith, Graf, and Joensuu (1955).

At elevated temperatures the presence of adequate CO_2 pressure is not only necessary for the formation and/or preservation of dolomite and associated magnesian calcite within the dolomite stability field, but also for the formation and preservation of magnesian calcite outside that field. Indeed, in the latter case the *amount* of Mg substitution is dependent on CO_2 pressure. If carbonate rocks were thermally metamorphosed under conditions permitting escape of CO_2, the resulting calcite should be virtually free of Mg.

A rough extrapolation of the curve of Fig. 4 to earth-surface temperatures indicates that the stable magnesium substitution in calcite crystallized in sedimentary environments should be very small.

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* In the presence of other components capable of reaction with dolomite, decomposition can, of course, take place at lower temperatures (see, for example, Bowen, 1940).

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On some factors affecting the chemical composition of Swedish fresh waters

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ABSTRACT

An attempt is made to relate variations in the chemical composition of Swedish fresh waters (mainly analyzed by Lohammar, 1938) to topographical, geochemical, and biological factors. The following are among the more general conclusions:

(1) In Uppland lake waters, and certain of those in Dalarna, total salt concentration is clearly related to altitude.

(2) There are distinct differences in ionic proportions between richer and poorer lake waters in both Dalarna and Uppland. In Dalarna the preponderance of moraine or Dalälven river sediments appears to be the important factor. In Uppland the high proportions of Cl, Na, and Mg in the waters of the lowest and richest lakes bear witness to the marine submergence of the district at the end of the glacial period.

(3) A comparison of Dalarna drainage and seepage lakes reveals that the waters of the latter are proportionally very rich in K but low in Ca. It is suggested that this may be due to a lesser degree of biotic influence on the waters reaching the seepage lakes.

(4) Dalarna seepage lakes exhibit low SO_4 levels in their waters, which may be connected with a slow rate of water transfer through them.

(5) The cations of bog waters are dominated by Na, those of fen waters by Ca. This illustrates the relative importance of atmospheric precipitation in the former, and mineral soil leaching in the latter.

(6) The frequency distributions of dissolved plus particulate minor constituents in fresh waters may be far from normal, low values predominating. Medians are therefore desirable in place of averages.

(7) Fe is most abundant in the more dilute waters, especially in Norrland. Mn is higher in the richer waters within each district, except in the Siljan area of limestone, where the lowest median occurs. Both elements tend to be highest (in respect of surface waters) in the shallower lakes.

(8) P is lowest in the Siljan limestone lakes, and highest in the Dalarna seepage lakes.

(9) N is lowest in the most dilute waters, Norrland being particularly low, and higher in the richer waters within each district (except in the Siljan area).

(10) Sr, which like the major constituents is highly correlated with total ion concentration, forms a slightly larger part of the total ions in the more dilute waters, especially in Norrland.

Introduction

One of the largest and most complete bodies of data concerning the ionic composition of fresh waters is the treatise by Lohammar (1938) on *Wasserchemie und höhere Vegetation schwedischer Seen*. Lohammar's analyses have recently been examined in two interesting papers by Rodhe (1949 and 1951), dealing separately with the major and minor constituents of the lake waters. This author has divided the lakes of the three Swedish districts investigated by Lohammar into six groups, and calculated the correlation coefficients between the different ion concentrations and the specific conductivity of the water, which forms an estimate of the total salts in solution. The conclusion reached is that lake waters of the bicarbonate type exhibit a surprisingly constant composition as regards the major constituents, Ca, Mg, Na, K, Cl, SO_4, and HCO_3. This is believed to be the result of ionic exchanges between the dissolved ions and the colloidal systems of the soils and lake muds. Rodhe then sets up the average ion proportions of the river and lake waters of the world (Clarke, 1924) as a "standard composition" with which all fresh

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waters may be compared. For a range of total salt content from 15 to 350 mg/l, in the proportions of the "standard composition," curves are given relating individual ion concentration to specific conductivity. In this way a complete water analysis is not necessary for comparison, but only the concentration of the individual constituent and the specific conductivity of the water.

The total contents (dissolved plus particulate, in the unfiltered sample) of the minor constituents P, N, Fe, and Mn on the other hand, show little correlation with specific conductivity. This is believed to be due to (1) their largely un-ionized state, which is less affected by ion exchange, and (2) their low concentration, which is more affected by organism uptake, and in the case of Fe and Mn by reaction with the organic compounds in the water.

While Rodhe recognizes that regional peculiarities may lead to differences in ionic composition (as evidenced in his Figs. 14–21, 1949), he does not discuss this aspect of the matter. The present object, therefore, is to draw attention to certain systematic deviations from the "standard composition" of fresh waters; and where possible to relate them to geochemical, biological, or topographical factors. Some features of interest with regard to the minor constituents, and to other fresh waters, are also discussed.

Major Constituents

In considering Ca, Mg, Na, K, Cl, SO_4, and HCO_3, Rodhe deals chiefly with Lohammar's Uppland lakes, numbers 1–21. However, detailed examination of the Dalarna lakes is also of much interest. While the range of specific conductivity is less than in the Uppland series, the number of rather dilute waters is much greater, and certain points become apparent on this account. (It should perhaps be mentioned that, even so, the richer cultivated areas are over-represented in Lohammar's Dalarna material.) In addition, a number of seepage lakes lacking inflow and outflow streams are included among the Dalarna waters, and form an interesting contrast to the more abundant drainage lakes, which possess such streams.

Dalarna

Figs. 1–6 give the averages of Lohammar's analyses for the major constituents in the Dalarna waters, in relation to specific conductivity. All lakes from the Siljan area are marked as open triangles, whether seepage or drainage waters. The other seepage lakes are shown as crosses, and the other drainage lakes as dots. The curves inserted in the figures represent ionic concentration in relation to specific conductivity, for varying amounts of total salts in the proportions of the "standard composition."

If we look first at the drainage lakes outside the Siljan region, we see that up to a specific conductivity of about 75 the Ca values fall below the standard curve, while over 75 they are mostly above the line. In the Na figure the reverse is generally the case. It may also be remarked that none of the waters above a specific conductivity of 75 is (on the average) below pH 7, while several of the dilute waters are slightly acid.

We are here faced with a clear contrast. The dilute waters are often slightly acid, and are relatively rich in Na and poor in Ca. The more concentrated drainage

lake waters tend to be alkaline, are rich in Ca and relatively poor in Na. A priori one might well seek the reason for these differences in the underlying geology of the areas draining into the lakes; and similar variations in the ionic proportions

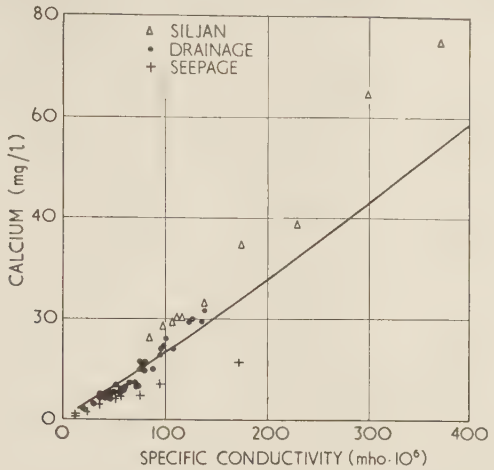

Fig. 1. Calcium in relation to conductivity in the Dalarna lake waters.

of fresh waters have in fact been ascribed to the differences between the drainage from igneous and sedimentary rocks (Conway, 1942). Pearsall (1921, 1922*a* and *b*) has also demonstrated differences in the ratio Na + K/Ca + Mg between

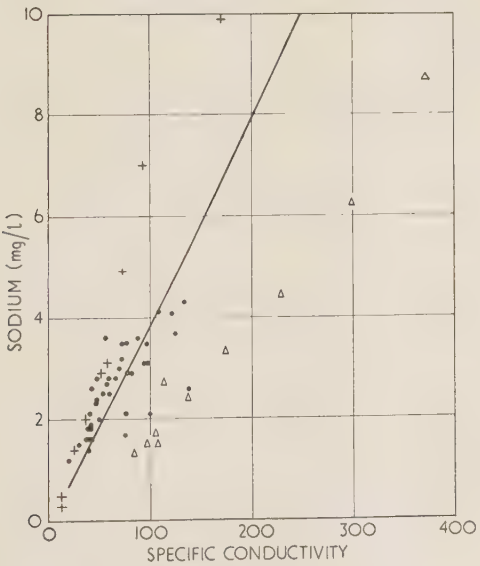

Fig. 2. Sodium in relation to conductivity.

rocky and silted lakes, lying partly in areas of volcanic rocks and partly in areas of sedimentary beds. The ratio is high in the rocky lakes, due chiefly to their low Ca levels. In the present instance, both the richer and poorer Dalarna lakes

outside the Siljan district appear to be surrounded by the same granites and gneisses, as far as one can tell from the map series Aa of the Swedish Geological Survey.

Also to be considered is the effect of dilution upon the partition of mono- and

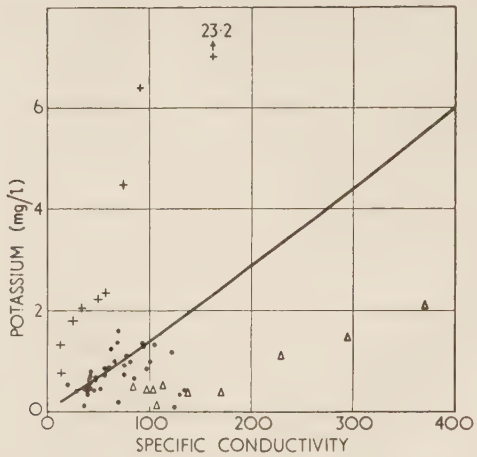

Fig. 3. Potassium in relation to conductivity.

divalent ions between adsorbed and solution phases of the soil-water system. Mattson (1942) has shown that adsorbed monovalent ions should be strongly displaced into solution by divalent ions as the system is diluted, and the ratio Na + K/Ca + Mg is in fact higher in the more dilute lake waters. However, this is due solely to a great decrease in the percentage of Ca; Mg on the other hand is

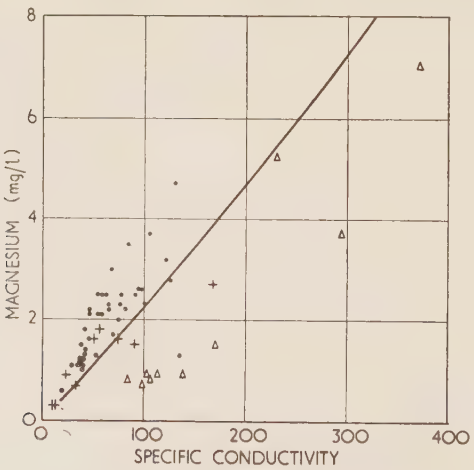

Fig. 4. Magnesium in relation to conductivity.

about as much higher in the dilute drainage lakes as are both Na and K (see Table 1).

In this case the main reason is probably to be sought in the glacial history and topography of the region. The poorer lakes lie in predominantly morainic upland

surroundings. Though some local sediments are present beside most of them, much of their drainage probably comes off glacial till. In contrast, the richer lakes lie mainly in the lowland sediments of the Dalälven river valley. (Two, numbers 58 and 77, do not. The first is influenced by nearby limestone, the second by lime-rich

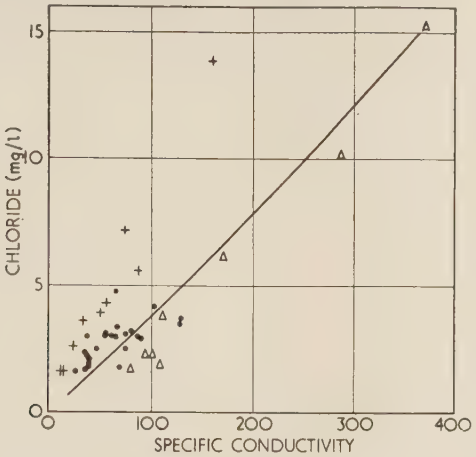

Fig. 5. Chloride in relation to conductivity.

Cambro-Silurian morainic material.) This distinction, between lakes chiefly draining glacial till, and those draining Dalälven sediments, is reinforced by another factor dependent upon it. Cultivation and settlement are both much more extensive on the river deposits than on the till, and therefore agricultural liming, other fertilization, and pollution will be of much greater importance in drainage

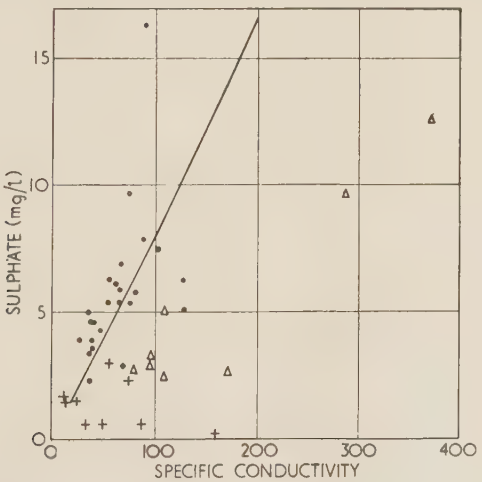

Fig. 6. Sulphate in relation to conductivity.

from the former. Whichever of these two factors exerts the predominant effect on water composition, it appears reasonable to separate this lake group into two, those above and those below a specific conductivity of 75.

We may next compare the average cation proportions of the four lake groups in Dalarna, as they are given in Table 1. (It should be pointed out that the Siljan lakes are much the same, whether of the seepage or the drainage type; and the seepage lakes outside the Siljan area are likewise similar, whether above or below specific conductivity 75. Lake 81 has been excluded as abnormal, cf. Lohammar, 1938. The following are the seepage lakes: numbers 26, 27, 29, 31, 46, 51, 59, 67, 79.) It is at once apparent that the poorer drainage lakes are proportionally higher than the richer ones in K and Mg as well as Na. However, the main feature

Table 1. *Ionic proportions in fresh waters, soils, and forests*

	Ca	Na	K	Mg	Cl/SO_4
	per cent of total Ca + Na + K + Mg *by weight*				*ratio*
River and lake waters, world average[1]	64	18	7	11	0·47
Uppland drainage lakes, 4–21	69	16	4	11	0·52
Uppland drainage lakes, 22, 24, and 25	51	29	4	16	0·74
Dalarna drainage lakes, conductivity < 75	52	23	7	17	0·57
Dalarna drainage lakes, conductivity > 75	67	16	5	13	0·49
Dalarna lakes, Siljan limestone area	85	8	2	5	1·0
Dalarna seepage lakes	32	24	32	11	4·1
Ground water of a mid-Swedish podzol[2]	40	37	5	17	
Finnish snow[3]	14	48	20	17	1·5
Iron podzol, A horizon, mid-Sweden[4]	26	28	40	6	
Iron podzol, B horizon, mid-Sweden[4]	25	24	39	12	
Iron podzol, C horizon, mid-Sweden[4]	24	27	37	12	
Average pre-Cambrian granite of Sweden[5]	19	29	45	6	
Spruce forest[6]	78	2	11	8	
Pine forest[6]	64	5	19	12	

[1] Data compiled by Clarke (1924).
[2] Data of Troedsson (1952), iron podzol on leptite-gneiss moraine.
[3] Data of Viro (1953).
[4] Data of Tamm (1950).
[5] Data of Holmquist (1906), calculated by Daly (1914).
[6] Data of Ebermayer (1876), given by Troedsson (1952).

of the comparison is the extremely high K and low Ca of the seepage lakes outside the Siljan region. This latter district has on the other hand the most calcareous lake waters, with the lowest proportions of Na, K, and Mg. Since it is in fact an area of limestone, the proportion of Ca is not surprising.

A comparison of the Dalarna waters with the ground waters of a podzol, and with the composition of podzol soil materials and granites which predominate

over much of the country, raises points of some interest. Data are given for these too in Table 1, calculated from the analyses of Troedsson (1952), Tamm (1950), and Holmquist (1906). The interesting data of Viro (1953) on Finnish snow are also included. We see that the composition of the seepage lake waters is intermediate between those of the granite and podzol materials and that of the drainage lake waters. These latter are much higher in Ca, somewhat higher in Mg, and very much lower in K than either the seepage lake waters, the podzol soils, or the granite. The podzol ground water resembles the drainage lake waters in respect of Mg and K, but is intermediate between seepage and drainage lakes with regard to Ca, and exceptionally rich in Na.

It is now desirable to attempt some explanation of these differences, even though our present knowledge restricts this to purely tentative speculation. Comparing their relative migration rates from the original igneous rocks to river waters, Polynov (1948) claims that on physico-chemical grounds of the solubility of their compounds, the order of migration of the major cations should be $K > Na > Ca > Mg$. This view is based partly upon calculations by the Russian geochemist Fersman (unfortunately no reference is given), and partly upon the order of the ionic potentials of the elements (i.e., the ratio of ionic charge to ionic radius, Goldschmidt, 1937; cf. also Hutchinson, 1943, and Rankama and Sahama, 1950). However, Polynov states that in fact Ca shows the greatest migratory capacity, and K the least (cf. also Polynov, 1937; Conway, 1942, 1945). If Polynov's method of determining actual migration rates is applied to the present waters, the order is $Mg > Ca > Na > K$, with the rates for Mg and Ca very similar. This is a complete reversal of the theoretical order given above. We may note that of the four elements, Mg is by far the least abundant in the Swedish rocks. Reiche (1942) has also noted deviation from Polynov's theoretical and actual orders in some New World areas.

Polynov's technique for calculating the relative migration rates of different elements or ions is to compare their proportional concentration in igneous rocks and in river waters draining igneous terrains, assuming that all elements in the latter are derived from the former. For example, from Polynov's (1937) data, SO_4/Cl in igneous rocks $= 3{\cdot}0$, in rivers from such rocks $= 1{\cdot}7$; therefore mobility of SO_4 relative to $Cl = 1{\cdot}7 \times 100/3{\cdot}0 = 57$ per cent. While this method may be of some use with regard to the cations, a serious error in the basic premise occurs in the case of Cl and SO_4, and vitiates at least partially Polynov's method of estimating migration rates. According to Conway (1942), almost all the Cl and SO_4 in river waters draining igneous terrains comes from sea-spray washed down in the rain. It is believed that the salts find their way into the atmosphere as droplets formed by the bursting of small bubbles (Woodcock *et al.*, 1953; Kientzler *et al.*, 1954) in foam patches formed either by high winds (Woodcock, 1953) or by the breaking of waves on beaches (Boyce, 1951). Now, much of the Cl and SO_4 in the ocean cannot have derived from rock weathering (Goldschmidt, 1954; Conway, 1942), and may well have come from volcanic emanation (Rankama and Sahama, 1950). Therefore the above method of calculating mobility cannot be used for these two ions.

Even with cations, it is difficult to evaluate the contribution to fresh waters

from cyclic salts in rain, though it has been very crudely attempted (Conway, 1942; Sverdrup, Johnson, and Fleming, 1942; see also Viro, 1953). While the cations may be presumed to have come originally from rock weathering, their return from the sea is unlikely to be in proportion to their delivery into it (cf. Rankama and Sahama, 1950). Nor can we expect them to be present in the proportions of sea-water, in view of the probable separation of salts in sea-spray during its evaporation. Japanese workers (Matsui, 1944; Miyake, 1948; Sugawara *et al.*, 1949; Koyama and Sugawara, 1953) have shown the SO_4/Cl and Ca/Na ratios of rain to increase greatly inland, and also with altitude of source. Their explanation is that evaporation of sea-spray separates crystalline $CaSO_4$, and to some extent $MgSO_4$, from hygroscopic NaCl particles. The latter can more easily form the nuclei of droplets, and presumably may be washed down in the rain more rapidly, while the latter may be carried like a fine dust farther inland. Dutch rain analyses also exhibit a rise in SO_4/Cl ratio inland, but some French data apparently show an opposite trend (see Eriksson, 1952). That rain and snow waters may vary widely in composition and concentration from one occasion to another has been demonstrated by various workers (Tamm, 1953; Viro, 1953; Gorham, unpublished). Lastly, it is necessary to separate the contribution of dust from that of sea-spray, which is extremely difficult even in non-industrial areas.

That sea-spray does provide an appreciable portion of the salts in rain seems likely from the above-quoted analyses. In this connexion, investigations of rain composition in progress at the Freshwater Biological Laboratory on Windermere have usually shown Na as the dominant cation, and the concentration of NaCl has been observed to rise sharply above the normal during westerly gales direct from the sea a few miles away. If sea-spray is important, its contribution to surface waters should not be ignored in calculating migration rates. Tamm's (1953) figures for Ca, Na, and K in rain falling in the open (Table 2) show concentrations of much the same order as those in the less-rich Dalarna lake waters, the differences being least in respect of K and greatest in respect of Ca. Allowance for rain evaporation would bring the levels even closer. Also, in the English Lake District the total salt concentration of upland tarns may differ very little from that of many rainwater samples (unpublished work in this laboratory). Moreover, Viro (1953) has calculated that for Finland as a whole, the material in precipitation is equal to about one-third of the total solids carried by rivers (including suspended matter). This proportion, admittedly based on a very few snow analyses, has also been calculated as 17 per cent for Ca, 30 per cent for Mg, 54 per cent for K, and perhaps about 99 per cent for Na. The SO_4 and Cl content of the snow, no doubt largely cyclic, appears to be more than equivalent to the sum of the four cations; and if NO_3 were added the anion excess would be even greater. The balance of cations is presumably made up chiefly of ammonium and hydrogen ions. The silica and sesquioxide contents of the snow are also quite appreciable, and probably derive from dust.

While the methods used to calculate migration rates have been shown to be extremely imperfect, it does seem likely that the major cations do not migrate in Polynov's theoretical order (see also Conway, 1945), and he ascribes this to the

intervention of organisms in the migratory process. Though of course discussion at the present stage must remain speculative, the situation with regard to the Swedish drainage and seepage lakes appears reasonably compatible with this view. The former, showing a much greater deviation from the ionic proportions of the granite, receive much water from streams draining surface-soil layers rich in both living and dead organic matter, and are much higher in Ca and Mg but lower in K than the seepage lakes. On the other hand the latter may be fed to a much greater extent by (1) little-altered rain as surface run-off (low in Ca and quite high in K —particularly if it has dripped through the forest canopy, see Table 2), and (2) slow-moving ground water long in contact with the deeper mineral soil horizons and rocks, and thus comparatively removed from biotic influence.

In this connexion it may be pointed out that the seepage lakes lie in deep pits along gravelly eskers, which form what may be described as subterranean streams. The gravels are usually of much the same mineralogical composition as the surrounding till, and their capacity to provide water is indicated by the fact that many Swedish towns pump their entire supply from such deposits (Sjörs, private communication). Some drainage lakes occupy similar sites; but since their waters do not show differences from the normal ionic composition of drainage lake waters, its may be inferred that the surface stream drainage is of predominant importance. (It should, however, be mentioned that the highest K concentrations occur in seepage lakes most liable to agricultural contamination; it is not known how significant this factor may be.) Lohuis, Meloche, and Juday (1938) have also found the residues of seepage lake waters in Wisconsin to be relatively rich in K, and to a lesser extent Na, as compared with the drainage lakes.

Although the seepage lake waters may be presumed to derive originally from surface precipitation, continued exchange during percolation through the deeper and wholly inorganic horizons of soil and rock might be expected to result in an alteration of their ionic proportions—toward those of a weathering medium unaffected by biological activity, in contact with the parent rock. Renick (1924) has previously suggested cation exchange during percolation as the factor responsible for the chemical differences between deep and shallow well-waters in Montana. There shallow wells yield hard waters rich in Ca and Mg, while the deeper wells give relatively soft waters proportionally higher in monovalent ions; at the same time total salts are much the same in both. Similar phenomena have been reported by Foster (1950).

Of course it is not to be expected that the ionic proportions of even pure water in contact solely with the parent rock should be the same as those of the rock itself. Different minerals, and their different components, do not all dissolve with equal facility. Moreover, as regards ion exchange between rock decomposition products and water, Bray (1942) has demonstrated that different ions are not all released from the adsorbed state with the same ease; and Mattson (1942) has illustrated the effects of dilution upon such a system.

In view of all these factors, it is a matter of some interest that detailed investigations should be made concerning the sources, paths, and rates of water supply to the seepage lakes; and the composition of the neighbouring soils and rocks as well. Information regarding the cations adsorbed by the various soil horizons

would also be most valuable. Much of the argument in these pages rests upon assumptions which, though perhaps reasonable, urgently require verification.

The high levels of Na in the podzol ground water shown in Table 1, together with the low proportion of Ca as compared with the drainage lakes, may well be due to the high demand of the forest for Ca and its low requirement of Na. This too is exemplified in Table 1, from data of Ebermayer (1876). Troedsson (1952) states that this ground water lies only one to two metres beneath the soil surface, so that a strong biotic effect seems likely. If the podzol ground water is in fact

Table 2. Ionic composition of rain and bog waters

Sample and location	*Number of samples*	Ca	Na	K
		mg per litre		
Rain in open sites[1]	25	0·43	0·59	0·30
Rain beneath spruce and pine[1]	36	1·57	1·86	5·26
Ratio *beneath trees/open sites*		3·7	3·2	17·5
Water from pools on raised bogs[2]	9	0·29	0·80	0·23

[1] From analyses of Tamm (1953) in Uppland.
[2] From analyses of Witting (1948) in Uppland.

drawn on to a greater extent by organisms than are the drainage lake waters, the result described above seems reasonable. It would also suggest that the dead residues of the biosphere are the most active agents in Ca liberation; presumably the humus acids (including biologically produced carbonic and sulphuric acids, cf. Robinson, 1949) could fulfil this role.

The marked reduction of K in the podzol ground water and in drainage lake waters, as compared with the seepage lake waters, snow water, podzol soils, and granite, is probably due largely to fixation of K in non-exchangeable form by colloidal clay minerals (cf. Levine and Joffe, 1947). Fixation in sandy podzols and brown podzolic soils appears to be most active in the colloid-rich horizons (Joffe and Kolodny, no date); which may be said to have developed mainly as the result of biologically activated weathering and leaching (cf. Keller and Frederickson, 1952). Phosphate complexes of Fe, Al, Ca, and Mg also seem capable of fixing K (Joffe and Kolodny, 1937).

Ebermayer's (1876) data suggest that the K content of the forest is not very great, although many later workers claim a high demand for this element by plants. This contradiction may be largely due to differences in material or sampling. The analyses of Henry (1908, cited by Lutz and Chandler, 1946) point to a much greater Ca/K ratio in the stem, branches, and bark of trees than in leaves.

An interesting effect of the forest upon the cycle of K has been shown by Tamm (1953), and can be seen in Table 2. Percolation through the forest canopy can increase the salt content of rain about threefold in Na, fourfold in Ca, and as much as eighteenfold in K. How far this is due to leaching of the leaves, and how far to animal excrement, etc., is not known. In the open the rain is highest in Na, Ca is intermediate, and K is lowest—though by no means so low proportionally

as in the podzol ground water or the waters of the drainage lakes. Presumably a large part of the Na derives from sea-spray, and some of the Ca and K as well; but as mentioned earlier, the elucidation of dust versus sea-spray contributions is very difficult. After percolation through the forest canopy the ratio between the monovalent ions K and Na becomes much more like that in the living forest itself.

If we now turn our attention to the anions, the seepage lake waters are richer proportionally in Cl and poorer in SO_4 than those of the drainage lakes; and Cl

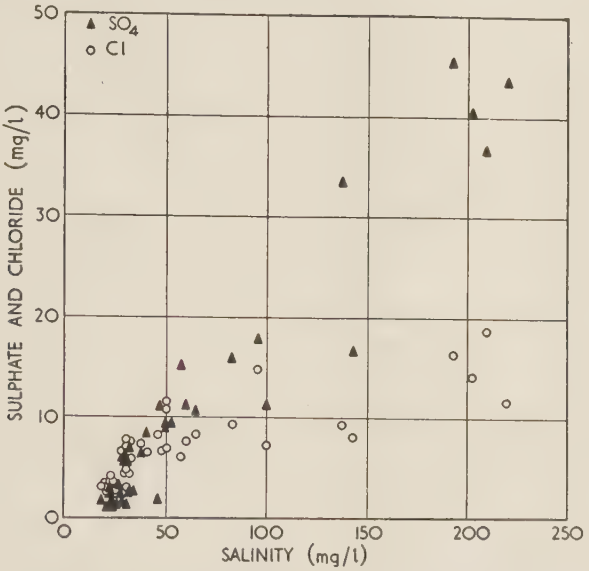

Fig. 7. The chloride and sulphate concentrations of Swedish river waters, in relation to total mineral content (data of Eriksson, 1929).

exceeds SO_4 in the former, while the reverse is the case in the latter. The waters of drainage lakes in Uppland, Norrland, and Skåne (Almestrand, 1951) also generally contain more SO_4 than Cl. This seems difficult to reconcile with the data of Eriksson (1929), which indicate that the majority of Swedish rivers carry more Cl than SO_4, especially in the north where soils are poor and both lake and river waters are extremely dilute. It is actually in these more dilute rivers that Cl predominates, in the most concentrated ones SO_4 is clearly in excess, as shown in Fig. 7. Conway (1942) has shown this to be a world-wide phenomenon. In Uppland SO_4 is well above Cl, while in Dalarna rivers it is only slightly less than Cl on the average, and yields a higher maximum value.

Swedish well-waters, which according to the data available are much more concentrated than river waters in the same area, also contain Cl in excess of SO_4 in most cases, but over the whole range of concentration (Arrhenius, 1952; since the data were provided by the public health service, waters suspected of contamination may be over-represented). The contrast between well and river waters is rather similar to that between seepage and drainage lakes, in that the

Cl/SO_4 ratio is higher in the former in both cases. It is of interest in this connexion that Rankama and Sahama (1950) claim chlorides as predominant in salt solutions from cavities in granites, and in mine-waters, in spite of the fact that rocks usually contain more sulphur than chlorine. The Finnish snow (Viro, 1953) also contains more Cl than SO_4.

In the Dalarna drainage lakes, the more dilute waters exhibit a higher Cl/SO_4 ratio, as might be expected by analogy with the rivers.

A factor which has a marked effect upon the SO_4 regime of many lakes is the oxidation-reduction potential of the mud-water system. Mortimer (1941–2) has demonstrated that through organic decomposition lake muds often become extremely reducing below; and that in shallow lakes during summer stratification, reducing conditions may even obtain at the mud surface, and in the bottom waters of the hypolimnion when oxygen is severely depleted. Under these conditions SO_4 may be reduced to sulphide, and if ferrous ions are also abundant and the pH is about neutral, black ferrous sulphide will precipitate. Dr. Lohammar informs me that ferrous ions are sometimes plentiful in the bottom waters of the Dalarna seepage lakes during summer anaerobiosis, and hydrogen sulphide may be also detectable by smell.

If biological sedimentation of sulphur to the bottom, and its anaerobic precipitation in the muds, is not counter-balanced by inflow replacement, SO_4 may be expected to reach very low levels (Beauchamp, 1952). This would be most likely in the seepage lakes, where water transfer may well be very slow. And those lakes with a rich plankton should be especially liable to SO_4 loss, in view of both the greater plankton sedimentation and the greater removal of oxygen through organic decay.

The Dalarna seepage lakes outside the Siljan area are in fact very low in SO_4, with a mean value of 1·3 mg/l and several analyses below 0·5 mg/l. This may be compared with a mean of 5·8 mg/l in the Dalarna drainage lakes, which are only slightly higher on the average in respect of total salts. Moreover, Lohammar (1938) has pointed out that SO_4 is particularly low in those seepage lakes with a large phytoplankton population. In this connexion Beauchamp (1952) has suggested that SO_4 deficiency may limit the productivity of some tropical lakes, especially below 0·5 mg/l.

It should be mentioned that seepage lakes elsewhere do not exhibit the same SO_4 impoverishment. In Uppland, overlain by calcareous marl, and in the Siljan district of Silurian limestone, seepage lakes are only slightly lower in this ion than drainage lakes of similar specific conductivity. It may also be remembered that these seepage lakes are not very different from their drainage counterparts with respect to the major cations either. The writer can offer no explanation.

Another possibility to be considered is that if lakes without inflow streams do receive most of their water by slow diffuse seepage through the lake muds (and this is a point deserving investigation), SO_4 could be removed from circulation there by reduction and precipitation as ferrous sulphide. On the other hand, such precipitation would not seriously affect the epilimnion of drainage lakes obtaining most of their water from surface run-off and percolation through the upper layers of the soil, into well-aerated inflow streams. The SO_4 level of the summer-isolated

hypolimnion in drainage lakes can of course be lowered by reduction, as Mortimer (1941–2) has shown.

The absence in May, July, and September data of any consistent summer fall of SO_4 in these Dalarna lakes needs study. Some much richer Uppland lakes with abundant rooted vegetation do exhibit a marked drop. With reference to this point, Ohle (1953) has suggested that fluctuations in ground-water level can strongly influence both the SO_4 and HCO_3 status of fresh waters. These ions may show a reciprocal relation in ground water, SO_4 rising with a rising water table and HCO_3 falling. The presumed explanation is that the sulphur compounds of soils (mainly sulphides of iron) may be oxidized to sulphuric acid and ferric hydroxide during periods of low water table when soil aeration is increased (see also Wiklander *et al.*, 1949, 1950*a* and *b*). The sulphuric acid will then react with bicarbonate salts to yield sulphates, water, and carbon dioxide. Thus when the ground water rises again it will be enriched in SO_4, which may wash out into the streams. Such a phenomenon might well have marked seasonal effects upon the inflow of SO_4 into lakes where the soils are rich in sulphur. Wiklander *et al.* (1949, 1950*a* and *b*) have shown that Swedish *gyttja* soils may in fact be rich in this element, occurring largely as sulphides of iron; and this is particularly true of the saline types. Thus a high sulphur content is a strong possibility in the areas of marine submergence in Uppland.

Many Norrland lakes are also low in SO_4, the mean value (excluding two "sulphate lakes," cf. Rodhe, 1949) is 1·9 mg/l. This low figure, however, reflects the general poverty of these waters in mineral matter: the proportion of SO_4 is only slightly below that of the "standard composition."

The correlation which often exists between a largely cyclic ion such as Cl and a mostly rock-derived ion like Ca is of some interest. Time may well be an important factor, allowing an increasing amount of material to be leached from the rock minerals into the percolating water, and also permitting evaporation, and consequently the concentration of all salts—including those thrown up in sea-spray and deposited on land by wind and rain.

Uppland

Some points of interest concerning the Uppland lakes may now be considered. Diagrams of ion concentration versus specific conductivity are given for lakes 1–21 by Rodhe (1949). These show a wide range of total salts, specific conductivity varying from about 20 to 600; but on the whole the Uppland lakes are much richer than those of Dalarna, and particularly those of Norrland.

A most interesting feature of the total salt concentration is its marked dependence upon the height of the lake above sea-level, as illustrated in Fig. 8. The north-westerly lakes, being higher, possess less salt. The dilute Dalarna lakes on glacial till and with specific conductivity less than 75 exhibit a similar dependence (see Fig. 8), again with a slight north-westerly decline. The marine submergence of Uppland and parts of Dalarna at the end of the glacial period may be an important factor here. Deposits of layered clay are found over a large part of the region, and calcareous marl is abundant east of a line from Gävle to the tip of Mälaren (cf. Swedish Geological Survey maps Ba 2 and Ba 5; also Lundqvist, 1935). At the

higher elevations the period of leaching, and presumably the leaching intensity (cf. Arrhenius, 1953) would be progressively greater. Another possibility is that in the uplands the amount of soil percolated by a given amount of rainwater on its way to a lake, and also the retention time within the drainage basin, may be less than in the lowlands.

Puke (1949) has reported a similar decline of specific conductivity with altitude in the lakes around Stockholm. However, at heights much the same as those recorded by Lohammar in Uppland, Puke's specific conductivity values are rather lower, owing probably to a lesser degree of submarine marl deposition in his more

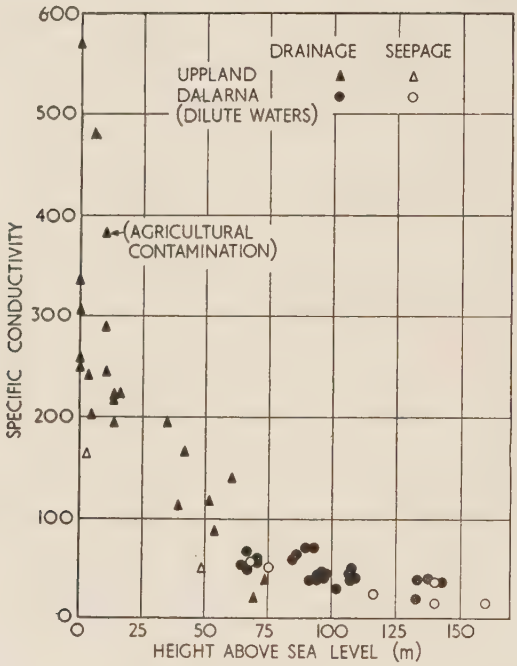

Fig. 8. The dependence of salt concentration upon height above sea-level, for all Uppland lakes and for Dalarna lakes on glacial till (i.e., below a conductivity of 75).

southerly localities. According to Arrhenius (1953), the mineral content of well-waters in Dalarna also declines in a north-westerly direction as the mountains are approached. The above trend is, however, absent among the richer Dalarna lake waters. Evidently the lime content of the Dalälven sediments, and/or the degree of agricultural liming, is a more important variable in these sites.

Correlated with dilution, there is also a tendency toward acidity in the more elevated Uppland and Dalarna waters. Ljunggren (1953) has likewise shown a greater degree of acidity in Värmland lakes above the limit of marine transgression, with a tendency for the more acid waters to occur in the northern districts.

Of the four richest Uppland lakes, three are especially high in Na, Mg, and Cl, and low in Ca. Since they are all very near sea-level, this richness in the chlorides of Na and Mg (see Table 1) is probably a relic of their submergence, not yet obscured by leaching. The fourth lake, number 23, is located at a slightly higher elevation,

and according to Lohammar (1938) may well owe its high salt content to excessive agricultural contamination.

It can be seen from Table 1 that the Uppland drainage lakes numbers 4–21 are very similar to their Dalarna counterparts, the drainage lakes above a specific conductivity of 75. Numbers 1–3 are below this value, and resemble the more dilute Dalarna waters. Lakes 3 and 10, although seepage lakes, do not show characteristics like those of the Dalarna seepage lakes.

Norrland

The Norrland lake waters are extremely dilute, and except for two "sulphate lakes" (cf. Rodhe, 1949) are comparable with the Dalarna drainage lakes influenced chiefly by glacial till. They are therefore low in Ca relative to the "standard composition," and high in Na, Mg, and K. Lohammar (1938) has noted a tendency to higher Na and Cl values nearer the coast, which may again be the result of a later emergence from the sea.

Swedish bogs and fens

Even more extreme deviations from the "standard composition" are observed in bog habitats. Witting (1947, 1948) has determined the cation concentrations of waters from a series of bog and fen-plant communities, separated according to the

Table 3. *Cation proportions and acidity of bog and fen waters in Sweden,*[1] *and in sea-water*[2]

Plant community	*Number of samples*	*Hp*	Ca + Na + K + Mg *mg/l*	Ca	Na	K	Mg
				per cent of total Ca + Na + K + Mg *by weight*			
Raised bog	43	3·9	3·3	16	58	11	15
Fen window in bog	14	4·6	4·0	27	53	6	14
Extreme poor fen	15	4·3	4·4	38	45	5	12
Poor fen	16	5·0	6·4	28	46	7	20
Transitional poor fen	8	5·9	9·7	64	24	2	10
Rich fen	4	6·1	10·9	59	29	3	9
Transitional rich fen	5	6·5	28·8	84	12	1	4
"Hällkar" poor fen near sea	11	4·4	34·0	8	70	4	19
Extreme rich fen	7	7·5	53·4	81	10	1	8
Sea-water		*ca* 8		3	84	3	10

[1] Calculated from data of Witting (1947, 1948).
[2] Calculated from data compiled by Clarke (1924).

phyto-sociological doctrines of Du Rietz (1949). The cation proportions and acidity of these are presented in Table 3, in order of increasing total content of the four cations. As a matter of interest the proportions of sea-water are included.

The bogs, which obtain their mineral supply solely by atmospheric precipitation, show extremely high proportions of Na. Moreover, in respect of the three cations

Na, Ca, and K, east Swedish bog waters are higher in the first and lower in the second and third than Tamm's (1953) rain water samples from open sites in east Sweden (see Table 2). Ca and K may be taken up by plants to a greater extent than Na. Also, Na will presumably be adsorbed by the peat colloids to a lesser degree than Ca (Mattson, 1942; Bray, 1942). Why K should be reduced to nearly the same extent as Ca (when compared with the rain) is something of a mystery in these wholly organic and doubtless phosphate-deficient peats, but more analyses are clearly necessary. Some data of Mattson and Karlsson (1944) suggest that the uptake of K relative to Ca may be greater than is indicated by Ebermayer's (1876) data for forest (see also Hutchinson, 1943). While the above authors only analyzed the green parts and twigs of the bog plants, the woody parts (presumably high in Ca and low in K) are undoubtedly much less important in bogs than in forest.

A notable feature of Table 3 is the marked replacement of Na by Ca as the richer fens are reached and pH rises. The balance between atmospheric mineral supply and soil leaching appears here very clearly. K and Mg tend to be low throughout, but are highest proportionally in the more acid sites. The acid but salt-rich "hällkar" poor fens are situated in rock pools beside the sea and receive much spray directly, which explains their high Na/Ca ratio. In solutions made up chiefly of chlorides and sulphates of sodium, acidity can develop unchecked even at high salt concentrations, which indeed tend to displace the hydrogen ions produced by organic decay into solution from the adsorbed state. In contrast, where high concentrations of calcium bicarbonate are produced by leaching of the mineral soil, humus acids are effectively neutralized.

Differences in ionic proportions such as these are probably of great importance in conditioning the distribution of plants in wet habitats. Some of their possible effects in nature have been remarked by Priestley and Hinchliff (1922; Hinchliff and Priestley, 1924) and by Pearsall (1922*a* and *b*; 1924). More recent studies have demonstrated the influence on plant growth (and presumably distribution) of varying ionic ratios in both culture solutions (Olsen, 1935, 1942, 1950, 1953) and the adsorbed phase upon soil colloids (Jenny and Ayers, 1939; Joffe and Zimmerman, 1944; Vlamis, 1949; Heslep, 1951; Epstein and Stout, 1951).

Minor Constituents

If frequency distributions are constructed for Lohammar's analyses of dissolved plus particulate minor constituents, they appear very far from normal. Low values predominate, but there are occasional very high ones. Therefore it is perhaps better to compare median levels instead of averages for the various lake groups. Such a comparison is made in Table 4, where all determinations from each lake in the group have been included, without averaging within lakes. While this method is open to criticism, the number of analyses is insufficient to provide reliable lake medians, and the general median is perhaps the best alternative. The medians have been obtained by intersecting cumulative frequency distributions at the fifty per cent level; and are only very approximate since the curves were fitted rather roughly by eye. Similar medians are given for specific conductivity within the lake groups, as an indication of total salts.

While Table 4 is not of course susceptible of complete explanation, certain points of interest may be remarked.

Table 4. Minor constituents (median values) in lake groups of Uppland, Dalarna, and Norrland

Lake group	*Specific conductivity mho* $\times 10^6$, *20°C*	Fe	Mn	P	N
		mg per litre		*µg per litre*	
Uppland drainage lakes, 4–21	200	0·25	0·026	41	300
Uppland drainage lakes, 22, 24, and 25	415	< 0·05	circa 0·035–0·040	41	high but extremely variable
Dalarna drainage lakes, conductivity < 75	45	0·18	0·020	20	240
Dalarna drainage lakes, conductivity > 75	90	< 0·05	0·033	20	340
Dalarna lakes, Siljan limestone district	115	< 0·05	0·008	12	220
Dalarna seepage lakes	55	< 0·05	0·020	45	230
Norrland drainage lakes, 101–165	25	0·83	0·019	20	110

Iron

The Norrland lakes are clearly much higher than any others in this element. This is no doubt due to the general base deficiency of the northern rocks and soils, which has led through acid leaching to mobilization of iron from the soil minerals, and the marked development of podzol profiles (Tamm, 1950). The low total salt content of the lake waters reflects this situation. In Dalarna and Uppland (also in Skåne, cf. Almestrand, 1951) the richer lakes tend to be lower in Fe, and the Siljan lakes are especially poor, with 31 of 33 analyses less than 0·05 mg/l. This last fact is presumably connected with the circum-neutrality of subsoils in this area. In spite of the usual poverty of limestone in Fe (Rankama and Sahama, 1950), the Siljan subsoils appear quite rich in this element (Arrhenius, 1953). It is not clear to the writer why the Uppland and Dalarna drainage lakes, differing widely in total salts, should have much the same levels of Fe and Mn, and show similar trends in relation to specific conductivity.

Not only are the poorer waters richer in Fe, there is also a greater deposition of lake and bog iron ore in poorer and more acid districts (Ljunggren, 1953). Thus the absolute difference between rich and poor areas with respect to iron leaching must be much greater than the differences in lake-water Fe suggest.

Outside Norrland it appears that only lakes less than five metres deep show Fe concentrations above 0·5 mg/l in the surface waters. Einsele (1938) and Mortimer (1941–2) have demonstrated that oxygen depletion during the summer may result in reduction of ferric complexes at the mud surface, leading to an escape

of divalent ferrous ions from the bottom, and a rise in Fe concentration in the lower levels of the water column. In the more shallow lakes this effect may penetrate to near the surface. Juday, Birge, and Meloche (1938) have similarly shown a marked increase of both Fe and Mn with depth in Wisconsin lakes, associated with a fall in oxygen and a rise in carbon dioxide. Turbulence may also result in stirring up precipitated ferric hydroxide from the mud surface to the upper levels of the water column in the shallower lakes.

The last-mentioned authors further state that Fe is higher in wells than in lakes from the same area. The Dalarna seepage lakes, which might perhaps be expected to show a similarity here, are low in Fe at the surface, possibly because better aerated. However, Dr. Lohammar informs me that they are sometimes rich in Fe in the badly aerated deeper layers.

The effects of oxidation-reduction conditions upon iron may also be of importance in connexion with the concentrations of rarer elements in lake waters. Goldschmidt (1937, 1954) has suggested that in the sea many of the rare elements such as Se, As, Pb, Sb, and Bi are removed from solution by adsorption upon oxidized ferric colloidal complexes. He claims that in this way the possibly harmful biological effects of many poisonous substances are minimized. It would be of great interest to know how far this process operates in fresh waters, and whether summer reduction of ferric hydroxide and other complexes at the mud surface may have unsuspected effects upon fresh water organisms, at least in or near the mud. Since many trace elements may be beneficial in small amounts while toxic at higher concentrations, the effects might well be extremely variable. While positively charged ferric sols adsorb anions, negatively charged manganic sols can adsorb cations. For instance Mo, B, Co, Ni, Cu, Zn, Tl, Pb, W, etc., may concentrate in Mn sediments. Ferric organic complexes may of course have dual adsorptive powers (Mattson, 1938; Mortimer, 1949).

Strongly reducing conditions, under which Fe may precipitate as ferrous sulphide, may also bring about the precipitation of a number of rare elements, such as Pb, Cu, Zn, Mo, Tl, V, Co, Ni, etc. (Goldschmidt, 1954). This too may have important biological consequences in fresh waters.

Manganese

This element, like Fe, exhibits very low concentrations in the Siljan limestone lakes, though the subsoils and limestones are quite rich in Mn (Arrhenius, 1953). Again, the high pH of the subsoils may be responsible. However, Dr. Lohammar informs me that lake number 80 is very rich in Mn in the deeper and probably badly aerated waters. Apart from the Siljan district, Mn tends broadly to show a trend opposite to Fe, being slightly lower in the poorer and higher in the richer lakes within the three geographic regions. Since the amount of Mn in granites is very much less than that of Fe (Arrhenius, 1953), the poorer soils and waters may be depleted of more soluble forms of this element. The data suggest that the compounds of Mn formed during weathering may be as a rule more stable in solution than those of Fe in lakes with a high salt content. There is some indication that the highest Mn values, like those of Fe, occur in shallow lakes.

With regard to bogs and fens, Witting's (1947, 1948) data show only low Mn

values ($< 0{\cdot}011$ mg/l) in waters above pH 6·5. Greater amounts are most likely in the pH range 4–5 (median roughly about 0·025 mg/l), though five of the six highest individual figures come from fens between pH 5·5 and 6·5.

Phosphorus

Here again the Siljan lakes are low, in spite of a moderately good supply of citric acid-soluble P in the subsoils (Arrhenius, 1953). The presence of abundant subsoil calcium carbonate, and the associated high pH values, may well account for a low water solubility of phosphorus. The Dalarna seepage lakes are highest in total P, being more than twice as high as the drainage lakes in this area. This may be due both to a greater degree of direct biological removal from the waters reaching the latter, and to fixation (as in the case of K) in those horizons of the soil which are rich in colloids as a result of intensive weathering and leaching under biotic influence (Hutchinson, 1952; Robinson, 1949). Undersea precipitation of calcium phosphate (cf. Rankama and Sahama, 1950) during the marine submergence of Uppland may well have enriched the soils of the marl areas. This, plus a greater amount of agricultural contamination, and also a shorter period and lesser intensity of leaching, may be responsible for the rather high P levels of lakes in the province.

Nitrogen

The Norrland lakes contain the least N. This is probably a result of low organic production, which might be expected from the northerly location, and from the poverty of the rocks in soluble salts—reflected in the dilute character of the lake waters. The next poorest group is that of the Siljan region, though the lakes there are not significantly different in this respect from the other Dalarna lakes, except those on Dalälven sediments. While not poor in total salts, the deficiency of P in the Siljan waters, coupled with the low proportions of other cations in relation to Ca, may perhaps limit biological productivity. It is noteworthy that the N/P ratio is highest in the Siljan lakes, with the richer Dalarna waters running a close second. The higher figures for N tend to come from lakes richer in salts, though as Rodhe (1949) has shown, the relation is extremely variable.

Strontium

Rodhe (1951) has proved that Sr, though present in small quantities, is strongly correlated with specific conductivity in the three geographic regions. He suggests that this is so because of its occurrence on the ionized form, and its lack of participation in biotic metabolism (see, however, Hutchinson, 1943; Odum, 1951). In addition, it may be remarked here that at lower levels of specific conductivity Sr accounts for a slightly larger part of the total salts, particularly in Norrland. The richest Uppland lake, number 25, has an exceptionally low percentage of Sr in its salts.

The ratio of Ca to Sr in these waters is also not without interest. It ranges from about 100 to 2,000, being lowest in the dilute waters, especially those of the north. With the exception of lake nember 165, this ratio does not exceed 450 in Norrland. The highest ratio comes from the most concentrated water, lake number 25 in Uppland.

Using the average Ca content of Holmquist's (1906) average Swedish granite, and Lundegårdh's average Sr content of Swedish igneous rocks (Rankama and Sahama, 1950, Table 15.1), the Ca/Sr ratio works out at about 90. Therefore Sr appears to be notably impoverished relative to Ca in many waters, presumably owing to the lower solubility of its carbonates and sulphates. The Ca/Sr ratio of limestone (from Table 5.52 of Rankama and Sahama, 1950) is about 400–700, a range surpassed by many of the values recorded for the richer Swedish waters, including some from the Siljan limestone district.

From the data of Witting (1947, 1948) it appears that a similar situation exists in bogs and fens. In the composite group "bogs to transitional poor fens" the median for the Ca/Sr ratio lies somewhere about 300; while in the "transitional rich fens" and "extreme rich fens" the ratio ranges from about 650 up to 2,550. The "hällkar" poor fens receiving direct sea-spray ranges between 60 and 160. According to Goldschmidt (1937) and Rankama and Sahama (1950), Sr is strongly enriched relative to Ca in sea-water (Ca/Sr ratio = 31). If, as Odum (1951) claims, the Ca/Sr ratio in shells is about the same as that in the aquatic environment over a series of concentrations, the lowering of the ratio in the ocean must be non-biological, and due presumably to inorganic precipitation of Ca, which of course is much more abundant than Sr. The high ratios of the richest Uppland lakes, which still show traces of marine submergence in their high proportions of Na and Cl, are rather interesting in view of the low ratio in sea-water. The anomaly is probably due to re-solution of calcium carbonate of high Ca/Sr ratio, deposited during the submergence.

The "poor fens" of Aneboda seem also to have Sr enriched relative to Ca, with Ca/Sr ratios varying from about 50 to 120.

Concluding Remarks

It can be seen from the above discussion that much of the variation in chemical composition of Swedish fresh waters is susceptible of explanation in terms of topographical, geochemical, and biological factors. While it is of course impossible at present to answer with certainty many of the questions raised here, it is hoped that these speculations may at least serve to focus attention upon some of the problems posed by Lohammar's invaluable series of analyses.

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The Pb^{207}/Pb^{206} ages of some stone meteorites

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ABSTRACT

The isotopic compositions have been determined for the leads isolated from three stone meteorites. Based upon certain assumptions, Pb^{207}/Pb^{206} ages of about $4{\cdot}5 \times 10^9$ years are calculated for the meteorites. The lead data indicate that the concentrations of uranium should be about 0·1 p.p.m. and the concentrations of thorium should be about 0·5 p.p.m. in stone meteorites.

Leads have been isolated from three stone meteorites and the isotopic compositions have been determined, using procedures described elsewhere (Patterson, 1951; Tilton *et al.*, 1954). The isotopic compositions and the concentrations, determined by isotope dilution, of these leads are listed in Table 1.

Table 1. *The concentrations and isotopic compositions of lead in stone meteorites*

Meteorite	Pb *conc.* (*p.p.m.*)	Pb *composition* 206/204	207/204	208/204
Forest City, Iowa	0·4	19·27	15·95	39·05
Nuevo Laredo, Mexico*	0·7	50·28	34·86	67·97
Modoc, Kansas	0·9	19·48	15·76	38·21

* An unrecorded find kindly supplied by Prof. Hermion Larios, University of Mexico. The 500-gram sample was found near Nuevo Laredo, Tamaulipas, Mexico, in 1950. It is a chondritic howardite with only a few chondrules. The metal content is much less than 1 per cent, and there is no evidence of oxidized iron, suggesting the absence of lawrencite. The sample had a complete fusion crust.

The lead isolated from the Nuevo Laredo stone is unlike any lead found in the crust of the earth. It corresponds to the lead one would expect to find in a slightly radioactive mineral formed about $4{\cdot}5 \times 10^9$ years ago. The lead in each of these stones may consist of two parts: that which was originally present when the stones were formed, and that which has been generated by the decay of uranium and thorium in the stones since they were formed. It may be assumed that this original lead had the same isotopic composition as the lead which has been isolated from iron meteorites, $Pb^{206}/Pb^{204} = 9{\cdot}50$, $Pb^{207}/Pb^{204} = 10{\cdot}36$, $Pb^{208}/Pb^{204} = 29{\cdot}49$.* On this basis, if the original lead is subtracted from the total lead in each stone, the remaining radiogenic lead may be used for the calculation of Pb^{207}/Pb^{206} ages. Despite an extreme variation among the isotopic compositions of the total leads, the calculated ages listed in Table 2 agree closely for the three stones.

Wasserburg and Hayden have recently determined the A^{40}/K^{40} ages of two stone meteorites (one of the meteorites was Forest City) using the isotope dilution

* These are the mean values for the two leads isolated from Canyon Diablo and Henbury troilite. These values differ slightly from the published values because they include a correction for spectrometer discrimination which was not applied to the published values.

method (WASSERBURG and HAYDEN, 1955), and have obtained values which agree within experimental error with the Pb^{207}/Pb^{206} ages reported here. In a strict sense this agreement only establishes an interdependence of the validity of two assumptions; namely, that the meteorite lead data have been correctly interpreted and that there has been no loss of A^{40} from the stone meteorites. A reasonable view

Table 2. Pb^{207}/Pb^{206} *ages and required* U *and* Th *concentrations*

Meteorite	*Age* ($\times 10^{-9}$ *yrs*)	U *conc.* (*p.p.m.*)	Th *conc.* (*p.p.m.*)
Forest City	4·5	0·06	0·2
Nuevo Laredo	4·6	0·2	0·7
Modoc	4·4	0·1	0·5

for the present would be that about $4{\cdot}5 \times 10^9$ years have elapsed since the formation of iron and stone meteorites. This age agrees with the age of the earth calculated from the differences between iron-meteorite lead and recent terrestrial lead (PATTERSON, TILTON, and INGHRAM, 1953, 1955).

Because of the manner in which the analyses were performed, the lead-concentration values reported here are considered to be lower limits of the true values.* Using the observed lead concentrations and a decay period of $4{\cdot}5 \times 10^9$ years, the minimum required concentrations of uranium and thorium have been calculated and are listed in Table 2. These required concentrations of uranium and thorium are an order of magnitude greater than the values we have previously regarded as acceptable (PATTERSON *et al.*, 1953; DAVIS, 1950), and are more nearly those reported by CHACKETT (CHACKETT *et al.*, 1950). Should these high concentrations of uranium and thorium be typical for most chondrites, several important consequences follow:

(a) The slope of the cosmic elemental abundance curve in the highest mass region approximates zero and does not have the large negative value which was recently reported (PATTERSON *et al.*, 1953).

(b) If the mantle of the earth were made of material similar to chondritic meteorites, the amount of heat generated by radioactive processes in the mantle would be about four times greater than the amount of heat currently believed flowing through the earth's surface from the interior.

(c) Since the relative concentrations of lead, uranium, and thorium in stone meteorites and in the crust of the earth are very similar, no extreme differentiation between lead and uranium within the earth is to be expected, and an estimate for the rate of differentiation of the earth's mantle (PATTERSON, TILTON, and INGHRAM, 1955), based upon a postulated extreme differentiation between lead and uranium, is invalid. The radiogenic lead which TILTON and co-workers have found

* The samples were first dissolved and then equilibrated with isotope tracer. At extremely low concentrations, losses resulting from the adherence to platinum and glass surfaces may be excessive. The previously reported concentrations of uranium in stone meteorites, which have been determined by the isotope dilution method, are also considered to be lower limits. Preliminary determinations of the concentrations of uranium and thorium in the meteorites studied here give values comparable to those listed in Table 2, but the problem of complete equilibration with tracer has not yet been solved.

in recently exposed ultrabasic rocks (Tilton, Patterson, and Davis, 1954) and which supposedly originated deep within the earth, can therefore be more easily reconciled with meteoritic data.

The author is deeply indebted to his colleagues, especially M. Inghram of the University of Chicago and G. Tilton of the Department of Terrestrial Magnetism, Carnegie Institution of Washington, who have co-operated closely in this work. The isotopic analyses were determined in Inghram's laboratory at The Argonne National Laboratory. Tilton has improved the procedure for the determination of the isotopic composition of lead by introducing the use of lead sulphide on tantalum filaments. All isotopic analyses were made using this modified procedure. Work at the California Institute of Technology was supported by AEC Contract AT(11–1)–208. The courtesy extended by the Argonne National Laboratory is gratefully acknowledged.

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Determination of alkali metals in meteorites by a distillation process

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ABSTRACT

The method of analysis described is based on the volatilization of chlorides from silicates in an induction-heated crucible within a water-cooled jacket. In this way potassium and other chlorides which would react with a heated furnace wall are quantitatively recovered as a volatile product in a form suitable for measurement by flame-spectrophotometry without further chemical processing. The consistency of recovery of sodium and potassium from silicates initially containing less than 1 per cent and 0·1 per cent respectively is ± 3 per cent. This article primarily describes the estimation of alkali metals in meteorites, but spectrographic evidence is included showing that zinc, lead, and silver for example are also concentrated in the volatile product and are absent in the residue, as would be expected from thermodynamical reasoning.

The alkali metals in chondrites are shown to be much lower and less variable than suggested by Brown and Patterson. Analyses of potassium in meteorites by wet-chemical analysis are shown to be unreliable. Our results compare favourably with those obtained spectrochemically by Ahrens, Pinson, and Kearns. Alkali measurements are reported for carbonaceous chondrites and some achondrites. In the chondrites (exclusive of the carbonaceous chondrites) which showed no distinctly visible signs of oxidation (14), the average sodium was 0·70 per cent with all values between 0·66 and 0·74 per cent, and the average potassium 0·088 per cent with all values between 0·084 and 0·095 per cent. For all chondrites examined (21) (again exclusive of the carbonaceous chondrites) the average sodium was 0·67 per cent with all values between 0·47 and 0·74 per cent, and the average potassium 0·085 per cent with all values between 0·058 and 0·102 per cent. The carbonaceous chondrites are more variable and generally have lower concentration of sodium and potassium. The achondrites examined (4) are highly variable in composition.

Introduction

Since the observation that the contribution to radioactive heating of planets by K^{40} is of the same order as that from uranium, there has been considerable interest in more accurate estimates of the cosmic abundance of potassium.

The potassium concentration in the stony meteorites is quoted as 0·20 per cent by Rankama and Sahama (1950). This value was also obtained by Brown and Patterson (1947) from a statistical average of chemical analyses of ninety-four meteorites by a number of other workers. In their estimate, the silicate phase of such widely differing classes of meteorites as carbonaceous chondrites and chondritic achondrites were averaged with the chondrites. K_2O varied from a trace to 1·46 per cent, and yielded a mean K of $0{\cdot}20_9$, to which Brown and Patterson ascribed an accuracy of $\pm 0{\cdot}02_1$ on the basis of standard deviation. In the same way, Na_2O values from 0·17 to 5·08 per cent gave an average for Na of $0{\cdot}81_8$ per cent, with an accuracy ascribed to be $\pm 0{\cdot}05_6$ per cent.

It has long been known that the most common contaminants in analytical reagents are the alkali elements (Groves, 1951). This, coupled with the difficulties of precipitating small amounts of the alkalis quantitatively, throws considerable doubt on the accuracy of wet-chemical analysis of these elements when they are present as minor or trace constituents.

In the course of an evaluation of the potassium and rubidium in earth-rocks, Ahrens, Pinson, and Kearns (1952) measured the concentration of these elements

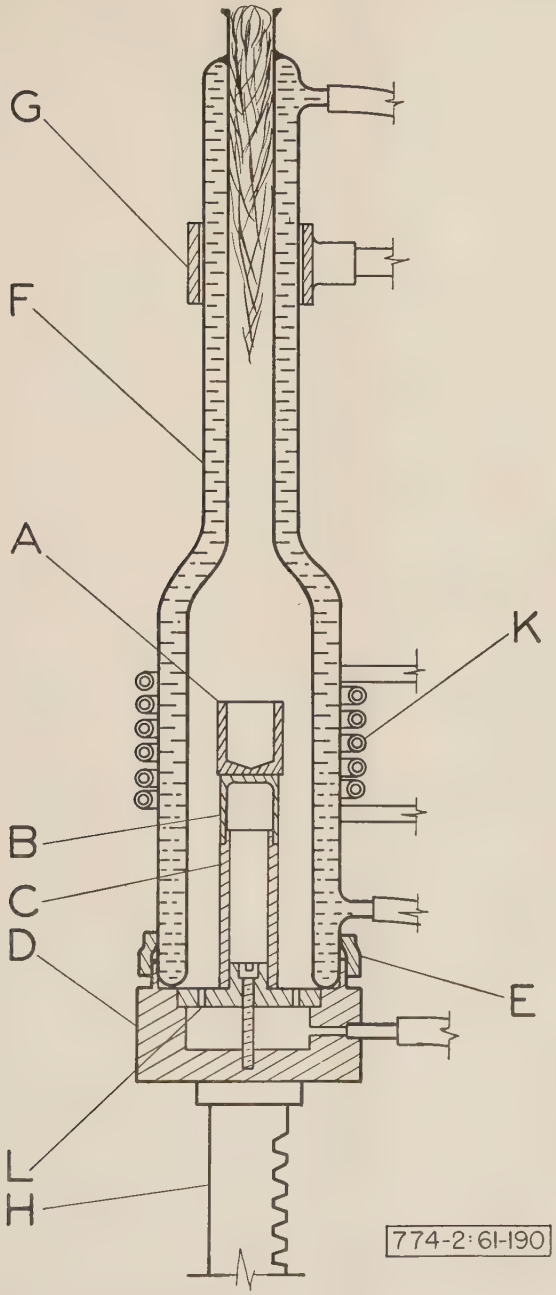

Fig. 1. Apparatus used for determination of alkali metals by distillation process. See text for description.

in twenty-one chondrites. They employed a spectrographic method with an external standard, and obtained values varying only between 0·05 and 0·13 per cent for K and 0·0005 to 0·0014 per cent for Rb. Their method is free from the contamination problems of wet-chemical analysis and should therefore be much more reliable. By confining their investigation to the chondrites (by far the most numerous group of meteorites available), the spread of values is immensely reduced compared to those of Brown and Patterson's survey. Ahrens, Pinson, and Kearns' average for potassium in the chondrites was 0·09 per cent. An error of +15 per cent and −10 per cent with occasional deviations of +33 per cent and −25 per cent, is ascribed by these workers to their results.

The method we have employed for determination of the alkali elements likewise eliminates the use of large quantities of chemical reagents. Our method is not limited to alkali analysis. We have simply applied the property of volatility under suitable conditions for isolation of the required element in place of solution and precipitation. It is well known that differential volatility has been used for some years in spectrography to improve measurements and levels of detection of the rarer elements. (See for example, Wedepohl [1953].) Fletcher (1949) has employed a volatilization procedure for the analysis of synthetic mixtures for lithium and of Bureau of Standards feldspars for sodium in the range of 10·73 and 2·38 per cent Na_2O. She heated the samples in a platinum boat to 1,200°C, and experienced difficulty in her potassium analyses because of the reactions with the boat.

To obtain quantitative recovery of reactive volatile chlorides of metals in trace or micro-quantities (e.g., the total mass of potassium from 1 gm of stony meteorite is usually less than 1·0 mg), it is important that they should not come in contact with heated surfaces after they have left the volatilizing zone. To satisfy this condition we have employed induction heating of a crucible inside a water-cooled container. More complete details of the method are given below.

Experimental

The apparatus employed is shown in Fig. 1. A graphite crucible *A* is supported on a pure alundum crucible *B*, which is upturned on the alundum tube *C*. The support is made in this way so that the alundum crucible in contact with the graphite can be renewed for each experiment. (Pure alundum crucibles type XN5 from the Morganite Company, New York, contain very low quantities of alkalis. All other crucibles tested contained appreciable amounts of alkalis.) The stand is rigidly fixed to a metal block *D*, which is sealed by the rubber ring *E* to the water-cooled "Vicor" jacket *F*. To facilitate opening and closing the apparatus, the Vicor jacket is clamped at *G*, and the crucible assembly and base are mounted on a rack and pinion *H*, by which they can be raised and lowered when access to the crucible is required. The graphite crucible is heated by current in coil *K*, from an induction heater. An inert gas is admitted through a ring of small holes *L*, and passes out of the apparatus at the top of the water-cooled jacket.

For the estimation of alkali metals in meteorites, one gram of the meteorite is finely powdered in a diamond mortar, mixed with 0·25 gram of powdered calcium chloride, and after drying for twenty minutes at 500°C is placed in position in the

apparatus illustrated. Nitrogen gas is circulated and a glasswool filter placed in the outlet gas-stream as shown. Cooling water is circulated in the jacket tube, and heating commenced.

We have attempted without complete success to utilize filters other than glasswool. Apparently the chloride particles in the outlet gas from the apparatus are electrically charged, so that they rather easily pass through a single layer of filter paper. Soxhlet extraction thimbles (paper, double weight for fat extraction) can be employed in place of glasswool, but are more readily clogged. Electrostatic precipitation proved ineffective, because the gas velocity is too great.

The temperature is raised sufficiently slowly to avoid ejection of solids from the crucible by the vapour evolution. For sodium and potassium chloride vaporization the crucible is maintained at 1,300–1,350°C for forty minutes, and then at 1,400–1,450°C for a further fifteen minutes. In experiments with mixtures of known potassium content (similar experiments are described below) it was shown that there is considerable latitude in the temperature and heating time within which no difference in recovery of the alkalis occurs. For example, heating at 1,200°C for one hour gave the expected potassium yield from silicates containing known amounts of the element. The yield decreased to 95 per cent when heating was carried out for one hour at 1,125°C. Sodium chloride is more volatile than the potassium salt, and even at 1,125°C there was no reduction of the yield.

The rate of the inert-gas flow through the apparatus is adjusted so that the vapour evolved as heating proceeds is forced to travel upward and condense on the cold Vicor wall above the crucible and on the glasswool. This avoids any reaction of the evolved chlorides with the alundum support column. The chlorides are carefully washed from the glasswool and interior of the water-jacket with dilute hydrochloric acid.

The solution so formed is collected directly in a silica beaker and at once evaporated to dryness. The solid is taken up in 5 ml of concentrated HCl, diluted to about 10 ml, and filtered through a Whatman No. 42 paper. Before use, the filter paper is washed several times with distilled water (from an all-metal distillation system) to remove residual alkalies in the paper. The solution is made up to 25 ml in a volumetric flask, and immediately transferred to a screw-capped polyethylene bottle for storage.

The potassium and sodium concentrations are estimated with a Perkin-Elmer flame spectrophotometer. This instrument is of the double-beam type, and measurements are made against an internal standard of lithium salt which is added to each solution. We have found it imperative to employ this type of machine. In earlier experiments with a single-beam flame spectrophotometer using an external standard we obtained results which we later showed to be quite erroneous. Using an external standard, it is not possible to simulate, in the standard solutions, all the constituents present in the unknown test solution in our case, and we have observed errors as great as 30 per cent in potassium estimations by this method.

In every case potassium salt is added to sodium standards, and vice versa, to compensate for their presence in the test solutions. The concentration of hydrochloric acid and added lithium ion in all solutions is adjusted to a constant value.

The final concentration of lithium ion in all solutions for flame-spectrophotometric use is 0·1 g/litre. In the solutions for potassium estimations, the lithium so added is about 2×10^3 times the concentration of lithium derived from the meteorite itself. In solutions for sodium estimations, the ratio of added lithium ion to that derived from the meteorite is 4×10^3.

For potassium estimations, 5 ml of the 25-ml stock solution is diluted to 20 ml to give a potassium-ion concentration less than ten parts per million. The flame photometer calibration (in presence of HCl and sodium ion) is linear to about 8 p.p.m. K, and only slightly curved up to 10 p.p.m. Blank experiments carried out in exactly the same conditions as normal estimations, but with no meteorite in the graphite crucible, show a potassium concentration of $0{\cdot}55 \pm 0{\cdot}05$ p.p.m. in the diluted stock solution. This is about 6 per cent $\pm$ 0·5 per cent of the potassium concentration from 1 g of chondritic meteorite.

In sodium estimations, 5 ml of the stock solution is diluted to 40 ml, giving a sodium-ion concentration less than 50 p.p.m. The calibration curve (in presence of HCl and potassium ion) is almost perfectly linear over this range. The sodium blank is $2{\cdot}05 \pm 0{\cdot}20$ p.p.m. in the diluted solution. This is approximately 6 per cent $\pm$ 0·25 per cent of the sodium concentration from treatment of 1 g of chondritic meteorite.

Rubidium can be estimated in the remaining 15 ml of stock solution. Only preliminary estimates of rubidium in certain cases are given here. A modified spectrographic method is employed, and results may deviate by $\pm$25 per cent because of the usual spectrographic limitations. The 15 ml of stock solution has to be concentrated to 1·5 ml. To facilitate this, all the metals to group IV of the standard wet-chemical procedure are first precipitated by bromine oxidation and addition of alkali-free ammonium hydroxide and ammonium carbonate solution. The ammonium hydroxide is made by bubbling cylinder ammonia into distilled water (from an all-metal system) in apparatus constructed entirely of polythene, and the carbonate by bubbling cylinder CO_2 through the ammonia solution.

To establish whether any rubidium might be lost by adsorption in the carbonates and hydroxides precipitated, a minute quantity of Cs^{137} (β emitter 0·5 MeV, thirty-seven years half-life) tracer was added. Within a counting accuracy of 5 per cent, all of the tracer was found in the filtrate and none in the precipitate in repeated experiments. As the cesium concentration is very much less than the rubidium, and the two ions would be expected to behave similarly, it appears certain that no appreciable adsorption of rubidium occurs in the precipitation. The need for multiple precipitations with consequent possible alkali contamination is thus eliminated.

The filtrate from the group IV precipitation is evaporated to dryness and the residue taken up in 0·5 ml concentrated hydrochloric acid and made up to 1·5 ml with distilled water. The concentration of rubidium is estimated with a Hilger grating spectrograph, using an internal standard of lithium. A burner like that used in the Beckman flame spectrophotometer is mounted on the spectrograph in place of the arc source. To obtain the necessary intensity of light, a 3-in. diameter 25-cm focal-length mirror is employed as a condenser. Under these conditions an

exposure of one to two minutes is required for solutions containing 2–3 p.p.m. Rb.

Before beginning meteorite analyses, a number of tests were carried out on the evaporation of chlorides from silicates to establish the efficiency of recovery of the alkalies. It was apparent that sodium chloride is evaporated completely in only twenty minutes at 1,200°C. Attention was thus concentrated on measurements of potassium recovery. Below 1,200°C the evolution of potassium chloride is slow. Evaporation at temperatures above 1,500°C gives rise to a product which difficult to filter. It may be that silicon monoxide is evolved, and this is undesirable, as it would yield colloidal silica in the final solution and this could affect the spectrophotometric measurements. An optimum about 1,350°C is indicated and the potassium is exhausted after thirty minutes. Temperatures were estimated with an optical pyrometer.

Tests were also carried out at intervals throughout the meteorite analyses to insure that the optimum conditions of recovery were maintained. The potassium in a chosen meteorite was measured a number of times and an average computed. An addition of Bureau of Standards feldspar No. 70 was made to the meteorite and the total potassium redetermined. The mass of feldspar added was 5–10 mg per gram of meteorite and it was weighed on a microbalance to better than 10 μg.

The results of these tests are grouped in Table 1.

Table 1. *Recovery of potassium from standard feldspar added to meteorites*

Name	*Average* K% *in meteorite**	K% *added as feldspar*	*Total* K%	K% *found*	K% *recovered*
Richardton	$0{\cdot}085_2$	0·0942	$0{\cdot}179_4$	$0{\cdot}173_8$	96·9
		0·0929	$0{\cdot}178_1$	$0{\cdot}178_4$	100·2
Holbrook	$0{\cdot}087_7$	0·0924	$0{\cdot}180_1$	$0{\cdot}182_6$	101·4
		0·0851	$0{\cdot}172_8$	$0{\cdot}176_0$	101·9
		0·0998	$0{\cdot}187_5$	$0{\cdot}193_4$	103·1
Forest City	$0{\cdot}084_2$	0·0889	$0{\cdot}173_1$	$0{\cdot}170_2$	98·3
		0·0788	$0{\cdot}163_0$	$0{\cdot}159_6$	97·9
		0·0904	$0{\cdot}174_6$	$0{\cdot}177_8$	101·8
		0·0920	$0{\cdot}176_2$	$0{\cdot}175_0$	99·3
		0·0980	$0{\cdot}182_2$	$0{\cdot}179_8$	98·7
		0·0777	$0{\cdot}161_9$	$0{\cdot}157_8$	97·5
		0·0874	$0{\cdot}171_6$	$0{\cdot}175_8$	102·4

* Richardton, average of 6 analyses, Holbrook and Forest City, average of 4 analyses each. See Table 2.

Note: Where more than two results are used for determination of averages in this and other tables the fourth decimal place has been retained. The maximum deviation is ±3 per cent and final values of the potassium concentration are quoted to the third decimal place.

It is clear that the recovery of the potassium in the added feldspar is complete to an accuracy of ±3·0 per cent. This included the uncertainty of potassium measurement in the flame photometer—approximately ±1·5 per cent. Mr. O. Joensuu of the Geology Department, University of Chicago, kindly examined a

number of residues of meteorites after volatilization of the chlorides, by the spectrographic method. Two specimens of Holbrook examined in this way showed a residue of approximately 10 p.p.m. K (based on the original one gram of meteorite). We have not corrected our analyses for this observed residue since this amount of potassium may easily have been picked up in grinding and preparing samples for the spectrograph. A specimen of Girgenti meteorite was analyzed by the evaporation method and the crucible replaced in the evaporation apparatus and the test repeated. No potassium was found in the second test. 0·25 g calcium chloride was added to the crucible and the experiment repeated once more. The only potassium recovered was that known to be present in the calcium chloride itself. Finally the residue was analyzed spectrographically. The potassium was less than 10 p.p.m. of the original sample.

Thermodynamically there is no reason why by this method the alkali metals should not be completely volatilized from the melted silicates as there is no potassium activity in the vapour over the liquid. Any residue is almost certainly only due to the difficulty of diffusion of the potassium from the centre of the silicate to the evaporating surface. For this reason in later experiments we have added 0·25 g of powdered graphite to the mixture in the graphite crucible to form a porous support for the melted silicate.

The results for sodium and potassium are shown in Tables 2, 3, and 4.

From Table 2 it is at once apparent that the chondrites are much more constant in alkali content than is suggested from published wet-chemical analyses. The arithmetic averages for Na and K are 0·67 and 0·085 with minima and maxima for Na of 0·47 and 0·74 and for K of 0·058 and 0·102. These potassium values are very much like those of Ahrens, Pinson, and Kearns for the chondrites. In Table 5 are shown comparative values for sodium and potassium by different methods of estimation. Within the limit of reproducibility of the spectrographic method, the Ahrens, Pinson, and Kearns values agree with ours except in the case of Forest City. The two potassium values obtained by G. J. Wasserburg and R. Hayden (1955) using the isotope dilution method are of special interest. The measurements were made on the same meteorite specimen as ours. The reproducibility in the isotope dilution measurements is believed to be about ± 3 per cent. It is striking that the two sets of results agree to better than 3 per cent.

The deviation of the wet chemical analysis results from all the others is evident. We are forced to conclude that for sodium and potassium concentrations of this order the wet chemical method is in general unsatisfactory. When a combination of flame-spectrophotometry and wet chemistry are employed with suitable blank corrections, sodium estimations at this concentration can be made with much greater accuracy than by the direct wet chemical technique. Dr. Wiik has conducted analyses on Holbrook and Ochansk in this way and the values are within 25 per cent of those reported here.

The suggestion by Brown and Patterson (1947) of high variations among the rarer elements is not borne out by our measurements and can be ascribed partly to unsatisfactory analysis and partly to the choice of averaging widely different groups of meteorites The average values, Na $0{\cdot}81_8$ and K $0{\cdot}20_9$, are accordingly erroneous.

Table 2. Sodium and potassium in chondrites

Name	Na%	*Average* Na%	K%	*Average* K%	*Average Ratio* Na/K
Allegan	0·74		0·087		
	0·75		0·087		
	0·74	0·74	0·085	0·086	8·6
Appley Bridge	0·73		0·089		
	0·72	0·73	0·087	0·088	8·3
Ausson	—		0·095		
	—	—	0·094	0·095	—
Baratta	0·69		0·089		
		0·69	0·090	0·090	7·6
Beardsley	0·67		$0·102_1$		
	0·67		$0·103_0$		
	0·66		$0·104_0$		
	0·66		$0·101_4$		
	0·66	0·66	$0·101_5$	$0·102_4$	6·4
Bjurböle	0·70		0·087		
	0·69		0·085		
	0·71	0·70	0·086	0·086	8·1
Colby	0·73		0·088		
	0·72	0·73	0·088	0·088	8·3
Densmore	0·58		0·072		
	0·59	0·59	0·071	0·072	8·2
Forest City	—		$0·085_6$		
	0·69		$0·083_6$		
	0·69		$0·085_8$		
	0·69	0·69	$0·081_7$	$0·084_2$	8·2
Forksville	0·69		0·086		
	0·68	0·69	0·083	0·085	8·1
Girgenti	0·70		0·091		
	0·69	0·70	0·093	0·092	7·6
Holbrook	0·73		$0·090_4$		
	0·72		$0·087_2$		
	0·73		$0·085_8$		
	0·74	0·73	$0·087_4$	$0·087_7$	8·3
Marion	0·69		0·086		
	0·63	0·66	0·087	0·087	7·6

Table 2 (continued)

Name	Na%	*Average* Na%	K%	*Average* K%	*Average ratio* Na/K
Mocs	0·72		0·092		
	0·68		0·089		
	0·72	0·71	0·092	0·091	7·8
Ness County	0·61	0·61	0·077	0·077	7·9
Ochansk	0·61		0·074		
	0·65		0·076		
	0·65	0·64	0·076	0·075	8·5
Pultusk	0·62		0·080		
	0·65	0·64	0·081	0·081	7·9
Richardton	0·73		$0·086_8$		
	0·71		$0·085_1$		
	0·71		$0·084_0$		
	0·72		$0·084_5$		
	0·70		$0·086_5$		
	0·70	0·71	$0·084_2$	$0·085_2$	8·3
Tennasilm	0·69		0·088		
	0·67	0·68	0·085	0·087	7·8
Tulia	0·47	0·47	0·058	0·058	8·1
Waconda	0·68		0·094		
	0·67	0·68	0·089	0·092	7·4
Averages		0·67		0·085	7·9

Table 3. Sodium and potassium in achondrites

Name and type	Na%	*Average* Na%	K%	*Average* K%	*Ratio* Na/K
Chondritic Achondrites					
Bishopville	1·04		0·085		
	0·96	1·00	0·081	0·083	12·0
Johnstown	$0·00_5$		$0·001_0$		
	$0·00_0$	0·003	$0·000_5$	$0·000_8$	—
Basaltic Achondrites					
Juvinas	0·31		0·038		
	0·34	0·33	0·037	0·038	8·7
Stannern	—		0·060	0·060	—

Table 4. Sodium and potassium in carbonaceous chondrites

Name	Na%	*Average* Na%	K%	*Average* K%	*Ratio* Na/K
Cold Bokkeveld	0·45		0·042		
	0·44	0·45	0·043	0·043	10·5
Felix	0·44	0·44	0·042	0·042	10·5
Haripura	0·52	0·52	0·060	0·060	8·7
Ivuna	0·56		0·057		
	0·56		0·055		
	0·56	0·56	0·058	0·057	9·8
Mighei	—		0·046		
	—		0·045		
	0·47	0·47	0·045	0·045	10·5
Mokoia	0·37		0·039		
	0·38		0·037		
	0·39	0·38	0·036	0·037	10·3
Murray	0·15		0·030		
	0·16		0·032		
	0·17	0·16	0·033	0·032	5·0
Orgueil	0·56		0·056		
	0·54	0·55	0·055	0·056	9·8
Average ratio					9·4

It is convenient at this point to compare our rubidium results with those of Ahrens, Pinson, and Kearns. We have carried out to date only a few estimations of rubidium, as an indication of the abundance of this element. The results, along with corresponding values by the spectrographic method (Ahrens *et al.*, 1952), are shown in Table 6.

Here the agreement of the values is less satisfactory. It would be necessary to make many more analyses before a critical discussion of the different values secured would be worth while.

A more comprehensive picture of the spread of values for sodium and potassium in the various groups of meteorites and their inter-relationships will be seen from the graph, Fig. 2, where all the observed values are plotted.

Fourteen of the twenty chondrites examined* fall in a cluster with sodium between 0·66 and 0·74 per cent and potassium between 0·084 and 0·092 per cent

* Ausson not included—no sodium analysis conducted.

Table 5. Sodium and potassium in some chondrites by different methods of analysis

Name	Na		K			
	Present method	*Wet chemical*	*Present method*	*Wet chemical*	*Spec.* (1)	*Isotope dilution* (2)
Holbrook	0·73	— tr.[4]	0·088	0·13[3] tr.[4]	0·08	—
Bjurböle	0·70	0·92[5] 1·05[4]	0·086	0·27[5] 0·30[4]	0·10	—
Forest City	0·69	0·60[6] 1·41[4]	0·084	0·05[6] 0·07[4]	0·05	0·083
Johnstown	$0{\cdot}00_3$	0·24[7]	$0{\cdot}000_8$	0·08[7]	0·001	—
Waconda	0·68	—	0·092	—	0·09	—
Barratta	0·69	0·45[8]	0·090	0·07[8]	0·12	—
Forksville	0·69	0·36[9]	0·085	0·22[9]	—	—
Beardsley	0·66	—	0·102	—	—	0·101
Mocs	0·77	—	0·091	0·19	0·11	—

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(maximum error ±3 per cent). The diagonal line through the centre of this cluster represents a constant Na/K ratio of 8·0 : 1. The only chondrite examined which does not fall on or quite near this line is Beardsley. This is a large specimen, apparently slightly oxidized, since the powdered sample was distinctly brown in colour. This stone was collected (Nininger and Nininger, 1950) more than a year after the observed fall and hence there was adequate time for contamination from surface water. The remaining five chondrites not in the main cluster all showed distinct visual signs of oxidation. Tulia exhibited signs of the most extensive oxidation. The specimen was almost uniformly the colour of iron rust. The specimen of Densmore was one of a group kindly sent to us by E. P. Henderson of the United States National Museum, Washington, D.C. He refers to this meteorite in a note accompanying the samples as follows:

Table 6. Rubidium in chondrites

Name	*Our method*		Ahrens *et al.*	
	Rb%	K/Rb *Ratio*	Rb%	K/Rb *Ratio*
Waconda	0·00040	170	0·001	90
Ausson, Girgenti *	0·00052	160	—	—
Ochansk, Holbrook *	0·00048	134	—	—
Forest City	0·00058	119	0·0006	85
Barratta	0·00060	150	0·0013	90
Average	0·00052	147	0·00085†	103†

* Mixture of equal amounts stock solution from the meteorites.
† Average value of all Rb measurements on chondrites by Ahrens, Pinson, and Kearns.

"The Densmore Kansas is a highly altered stone and because of its altered condition it has never seemed an attractive stone to study. But if you find that the alkalis are consistent in most of the meteorites (chondrites) it would be interesting to see what happens to them in cases of extreme alteration."

Our results indicate that in weathering, the sodium and potassium have been removed in amounts proportional to their original concentrations. This is contrary to what would be expected, the more likely effect being preferential leaching of sodium ion. A possible explanation is that the sodium and potassium are mainly feldspathic and that some of the feldspar is broken up in the weathering reaction and *all* the soluble constituents of the decomposed feldspar extracted. The position of Beardsley with respect to the other meteorites (Fig. 2) gives the impression that potassium has in some way been added to the meteorite in the course of weathering. This may have occurred during the year in which it was exposed to the weather. If Beardsley originally had the average concentration of potassium in the unweathered chondrites its age should be $\sim 2{\cdot}5 \times 10^8$ years higher than that calculated by Wasserburg and Hayden (1955).

If, as seems justifiable, we choose to neglect stones which show distinctly visible signs of having been altered since they reached the earth we have the average for sodium 0·70 per cent with all values lying between 0·66 and 0·74 per cent and for potassium an average of 0·088 with all values between 0·084 and 0·095 per cent (maximum error ± 3 per cent). The average Na/K weight ratio using these values is 7·96.

The carbonaceous meteorites give the most unexpected results. The results given in Table 4 are not immediately comparable to those of the chondrites because of the large amounts of carbonaceous and other volatile constituents, e.g., ~30 per cent by weight in the case of Orgueil. Dr. B. Wiik (private communication) has made careful analyses of Felix, Mighei, Cold Bokkeveld, and Orgueil. Using his values for silica, 33·95, 27·81, 27·33, and 22·56 per cent respectively and our analyses for sodium and potassium the atomic abundances for these elements relative to

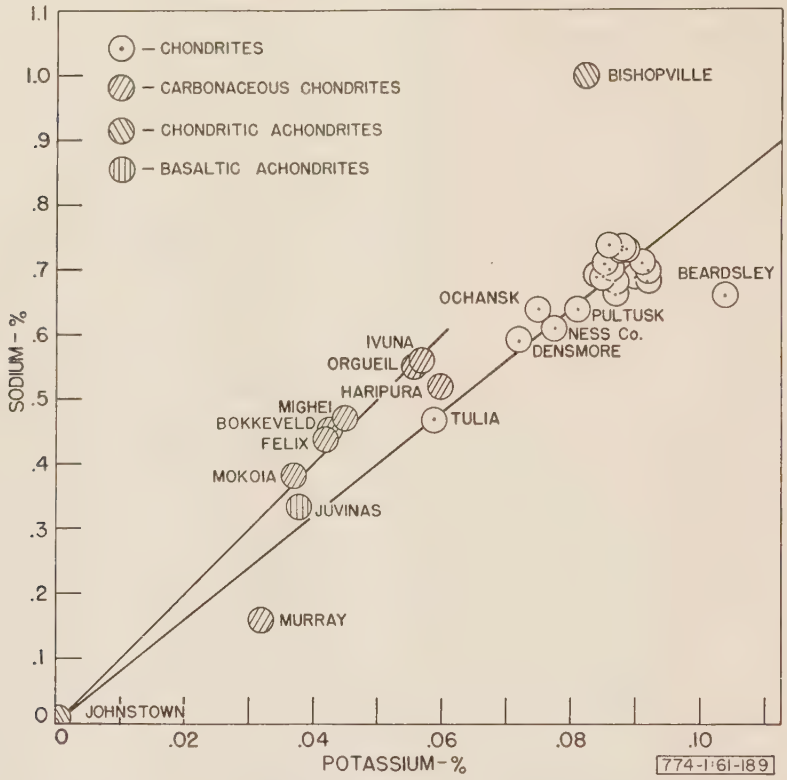

Fig. 2. Sodium and potassium content of various kinds of meteorites. Graphic representation of data in Tables 2, 3, and 4.

silicon taken as 10,000 are: Felix, 339 and 19; Mighei, 441 and 25; Cold Bokkeveld, 430 and 24; and Orgueil, 637 and 38. Superior analyses as selected by Urey and Craig (1953) exist for five of the chondrites of Table 2. Using the silica analyses for these meteorites and the analyses of this paper for sodium and potassium the atomic abundances for these elements are found to be: Girgenti, 459 and 35; Forest City, 506 and 36; Allegan, 508 and 38; Forksville, 472 and 34; Bjurböle, 445 and 32. It is evident that much greater constancy of composition exists among the chondrites than among the carbonaceous chondrites listed above. We have thought that the carbonaceous chondrites containing carbon compounds and water might be the primordial cosmic material which first accumulated to form objects

which in turn accumulated into the planets. However, we expected such primordial condensations to be of uniform chemical composition except for the volatiles and to give the cosmic abundance of the elements. These objects do not conform to these expectations with respect to sodium and potassium and Dr. Wiik's analyses show that this variability is true of other elements as well. Accordingly we do not regard the carbonaceous chondrites to be this type of material. It seems most likely that they are ordinary chondritic material which has been subjected to the action of water solutions in some way.

If for the moment we disregard Murray, the carbonaceous chondrites also lie on or near a line of constant Na/K ratio (10·0 : 1). This indicates that potassium was leached from this material more readily than sodium, which is not the case in terrestrial weathering processes. However, under strong reducing conditions ammonia and carbon compounds could be present and would change the relative solubilities markedly.

In view of the uncertainty regarding the amount of the carbonaceous chondrites which should be taken in estimating the average composition of cosmic solids, there is some uncertainty in the potassium concentration which should be used in calculations of heating effects within the earth and other planets, but a value in some measure less than 0·088 per cent is indicated.

The achondrites are highly differentiated objects and appear to have been crystallized from melted silicates. In such process partial separation of the elements would occur and hence it is not surprising that large variations occur even though we do not understand the particular variations observed. The materials of the achondrites appear to have been included in the chondrites, and we believe that the uniform composition of the chondrites is due to a great variety of materials, such as that of achondrites and irons, having been thoroughly mixed and incorporated into these objects. We believe the carbonaceous chondrites are chondritic material which has been modified by water solutions of ammonia and carbon compounds.

The method we have used here to separate the alkalis from silicate mixtures is applicable to a number of other metals. Mr. O. Joensuu of the Geology Department of the University of Chicago kindly made spectrograms of the volatile products and residues from the evaporations of chlorides from the meteorites Richardton and Holbrook. These show that gallium, zinc, lead, sodium, and silver are concentrated in the volatile portion and are absent in the residual solid. To ensure the detection of any elements in low concentration in the residues a larger sample was taken for the spectrogram of the residue and the time of arcing was increased with respect to the volatile product. None of the elements referred to were found in the residue.

We believe that the method may be applied to obtain tungsten, cadmium, and other metals with similarly volatile chlorides, in a concentrated and soluble form more conveniently analyzable by conventional methods than in the original silicate. We suggest that by addition of sodium carbonate to a silicate and evaporation at 12–1,400°C the chlorides might be obtained in a readily estimable form. We are already engaged in work in these fields and this will be reported in later publications.

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The ages of three stony meteorites and a granite

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ABSTRACT

The ages since solidification of the stone phases of three meteorites have been determined by the ^{40}K,^{40}A method. The ages* were between 1·9 and 3·8 $\times$ 10^9 years. By the same method the age of a granite has been found to be 4·9 $\times$ 10^8 years.

1. Introduction

The most extensive studies on the ages of meteorites have been made by Paneth and his collaborators (Paneth, 1953; Chackett *et al.*, 1953; Dalton *et al.*, 1953), who measured the amounts of helium, produced by the disintegration of uranium and thorium, in iron meteorites. This method of age determination cannot be applied to stony meteorites, for loss of helium from silicates may not be negligible (Hurley and Goodman, 1941); loss of helium from the iron meteorites is considered to be small (Paneth, 1939). Furthermore, in silicate meteorites helium is produced by cosmic rays (we have found 4·87 per cent ^3He in the helium from Akaba), and we cannot yet assess the relative amounts of helium produced by radioactivity and cosmic rays, though this can be done in iron meteorites (Dalton *et al.*, 1953; Martin, 1953).

An alternative method of age determination, depending on the decay of ^{40}K to ^{40}A, has two advantages over the helium method. The argon atom is larger than the helium atom, and so diffusion losses should be smaller. It also appears from the results obtained by us that cosmic-ray-induced spallations do not produce significant amounts of argon. Gerling and Pavlova (1951) have already used this method to determine the ages of two meteorites, Zhovtnevy Khutor, and Saratov, but they assumed, without mass-spectrometric investigations, that the argon from their samples was all ^{40}A.

In the analysis to be described argon was extracted from the minerals and the gas was examined mass-spectrometrically to estimate the quantity of radiogenic ^{40}A. Since only limited samples of the meteorites were available to us, methods were developed to assay micro-quantities of gas. Special attention was paid in the isolation and assay procedure to the possibilities of loss and contamination of the gas samples.

2. Experimental

Two methods were used for extracting the argon from the minerals—straightforward heating and solution in a flux. The argon was separated from other gases in a high-vacuum apparatus, in which oxygen was removed on heated copper.

* See note added in proof.

carbon dioxide by condensation, and nitrogen by reaction with barium vapour. Helium and neon were removed after fractional absorption on charcoal cooled in liquid nitrogen.

3. Mineral Decomposition by Heating in a Flux

The difficulties encountered in the use of fluxes have already been discussed by Lord Rayleigh (1939). Sodium carbonate was unsatisfactory because of the

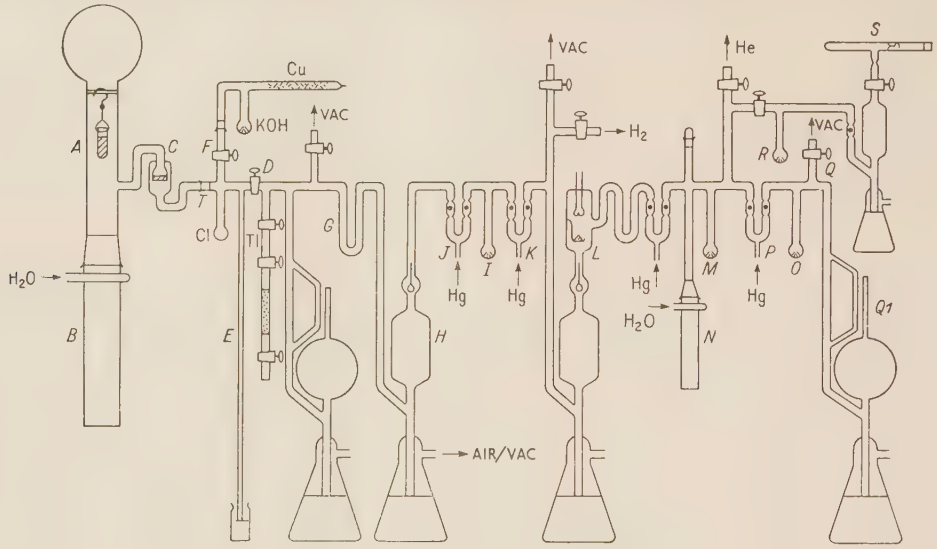

Fig. 1. Argon extraction apparatus.

large amounts of carbon dioxide liberated in a hot vacuum furnace, sodium hydroxide because large amounts of water were released into the vacuum system. Sodium peroxide was more satisfactory, in that the oxygen liberated at 480°C could be removed easily on heated copper at 360°C. Rafter (1950) has described the use of this flux in mineral decomposition.

The apparatus used in the flux method is shown in Fig. 1.

Blank determinations in the absence of minerals

In the early stages of this work it was found that 25 g of sodium peroxide could yield 6×10^{-4} cc of argon, and the method used in the estimations involved preliminary heating and "degassing" of the flux. The mineral specimens were then dropped into the molten flux. The volume of argon isolated, after blank determinations using this procedure, was approximately 5×10^{-5} cc. Results, with and without the empty Pyrex capsules used to hold the samples, were not significantly different.

Isolation procedure

The mineral specimen, ground to pass a 100-mesh sieve, was weighed into a very thin Pyrex glass vessel with a lid, and this vessel was suspended by an iron hook and a nickel wire in the vacuum bulb *A*. 30 g "AnalaR" sodium peroxide were placed in the stainless-steel tube *B* which was fitted to the apparatus and

evacuated slowly through the coarse sintered disc *C*. After twenty-four hours had elapsed, the tube was heated in a resistance furnace during the next three hours to 580°C; a considerable quantity of gas was produced and this was removed by the mercury diffusion and oil-pumps. Tap *D* was then closed and the iron hook was released with a magnet and the sample allowed to drop into the glowing molten peroxide; it was then heated to 730°C during the next three hours. A vigorous reaction and "boiling" could be seen in the furnace, and the mercury in the manometer *E* was observed to fall by 15 cm. The furnace was cooled and tap *F* opened to admit the gases released from the meteorite to a KOH pellet and to heated copper at 360–400°C. Trap *G* was cooled by liquid nitrogen, and those gases which remained were transferred by the Toepler pump *H* into the charcoal trap *I*, which was cooled in liquid nitrogen. Gases, including argon, which were adsorbed on charcoal were isolated overnight between the mercury ventils *J* and *K*. About twenty minutes were allowed for condensations of this kind on charcoal.

The gases were subsequently transferred into the small chamber *L*, which contained a KOH pellet and a spiral of copper wire which had been reduced by heating in hydrogen. This wire was heated to a dull red colour, electrically, and any traces of oxygen removed. After ten minutes of this treatment the gases were condensed on the charcoal in the trap *M*, which was cooled in liquid nitrogen, and then released into that part of the apparatus containing the steel furnace *N*. This furnace, containing barium metal, was heated to 800–850°C for ninety minutes for the removal of nitrogen, and then cooled to room temperature, and finally the gas remaining was condensed into the charcoal trap *O*. Ventil *P* was closed and the tap *Q* opened to the vacuum for two minutes, and thus any helium and neon in the gas sample were removed. Partition coefficients for helium and neon between the gas-phase and solid can be found in a paper by Glueckauf (1945). Trial experiments showed that argon was not lost in this process.

The argon, which was retained on the charcoal, was measured after expansion into the calibrated McLeod gauge *Q*1; a correction for the dead space was applied. The gas was retreated in the barium furnace and its volume was remeasured until constant results were obtained. The entire argon sample was then condensed on to the charcoal in trap *R* and allowed to expand into the Toepler pump in this section. The gas was then pumped into the sample tube *S* prior to mass-spectrometric examination.

The calibration of the apparatus and its proper functioning were checked by estimation of the argon in standard samples of air admitted from the pipette *T*1. The results obtained were 0·936, 0·936, 0·952 per cent (cf. the previously obtained value 0·93 per cent (Chackett *et al.*, 1950), and thema ss-spectrometric results for the air samples are shown in Table 1. It appears that there were no losses of argon in the purification process. It should also be mentioned that there was no application of Tesla discharges during the estimations.

4. Heating of Minerals without Flux

It could not be concluded from the results of a single extraction method that all the argon in the minerals had been isolated. A second method was used, however, and it was found that the results of both methods were in reasonable agreement.

A silica tube was attached to the standard joint T and the tube evacuated and heated to 400°C for two weeks. "Blank" determinations of argon without the mineral gave small amounts, viz., 3×10^{-5} cc s.t.p. Mineral samples were ground to pass a 100-mesh sieve, placed in a platinum boat, and inserted into the silica tube when the tube was at 200°C. The system was sealed and evacuated for two hours at 200°C. The silica tube was then isolated from the vacuum system and heated to 1200°C for four hours in a resistance furnace. Considerable volumes of gas were produced. Most of the gas was condensed in $C1$, a trap surrounded by liquid nitrogen, and the residual gases were Toepler-pumped into the purification and estimation train. Whereas initial heating of a mineral produced 4×10^{-4} cc s.t.p. argon, a second heating produced only $0{\cdot}8 \times 10^{-5}$ cc of argon in excess of the blank.

5. Mass Spectrometry

To assess the proportion of radiogenic ^{40}A in the meteorite samples it is necessary to subtract from the total argon yield the argon arising from other causes, atmospheric contamination, argon dissolved in the silicate, and argon from the chemical processing—the "apparatus blank." The necessary correction can be made after a mass-spectrometric analysis of the gas sample, if one assumes all of this contaminating argon to have an isotopic composition similar to that of the earth's argon; this we have assumed in our work. We would point out, however, that this assumption may not be valid. Nevertheless, despite the uncertain nature of the assumption, the errors involved in estimating the radiogenic ^{40}A are small, if the assumption is approximately true; this is because the quantity of contaminating argon is a fraction, in four cases out of eight less than 20 per cent, of the total argon yield; some runs have been discounted because of too much contamination. Furthermore, most of this contamination comes from the "apparatus blank," and where gas is extracted from the same meteorite sample by two different methods in which the "apparatus blank" contribution to the total argon yield is different, the mass-spectrometric correction provides a consistent radiogenic argon yield. We have in fact established, in experiments 1, 2, 4, and 5, consistency between the mass-spectrometric data and that of the quantitative gas analysis, in that these methods gave almost the same estimated percentage of "radiogenic" argon.

Because of the smallness of the gas samples available for analysis (10^{-4}–10^{-5} cc s.t.p.) it is necessary to correct for any small hydrocarbon- or HCl-contamination which may be present. All of the present samples were free of HCl, but some of them (Nos. 3, 6, 7, and 8) contained a trace of benzene (this solvent had been used on one occasion for cleaning taps on the extraction apparatus). From a knowledge of the benzene mass-spectrum, and by measuring all the peaks in the mass-range 35 to 41 inclusive, the measured mass-36 peak may be corrected for the hydrocarbon contamination. Applying this correction in the cases mentioned, yields of radiogenic ^{40}A consistent with those obtained from clean samples were obtained.

Since mass-spectrometric data for Monze could not be obtained, the age calculated is a maximum value.

The isotopic assay of the argon samples (10^{-4}–10^{-5} cc s.t.p. diluted in helium to 10^{-2}–10^{-3} cc for ease of gas-handling) was carried out in a Nier-type mass-spectrometer. The samples were contained in break-seal tubes. The overall

sensitivity of the instrument was such that an isotopic component of argon of less than 10^{-8} cc s.t.p. could be detected; the limitation on sensitivity was the residual background peaks at mass numbers 36 and 38.

The accuracy of absolute abundance measurements will depend upon the mass-discriminations in the ion source and in the ion-beam detector of the spectrometer. Discriminations in the former have been reduced to a minimum by removing all auxiliary fields, and employing magnetic scanning. A secondary electron multiplier with Be-Cu dynodes has been employed as a current preamplifier in the ion-beam detection arrangement, the positive ions impinging directly upon the first dynode. It is necessary to apply a correction, because of the "constant velocity" law of secondary electron emission, since the experimental conditions here are those of constant energy. This has been done empirically by running standard atmospheric argon samples at frequent intervals during the determinations. The precision of the mass-spectrometric measurements was certainly better than 5 per cent.

The method of measurement was a dynamic one, in order to allow most of the gas sample to be consumed during a measurement. Molecular-flow conditions existed throughout the entire gas-flow sheet, and the isotopic ratios measured at successive intervals of time have to be extrapolated back to the time of leaking in the sample. It was also necessary to check the whole gas-handling system for memory effects (which were much more in evidence for argon than for helium) and any small leaks, by observing the ^{40}A-peak over a period of time, before the sample tube was broken open. A detailed description of the methods will be published elsewhere.

6. Potassium Estimations

The method used was that described by Shapiro and Brannock (1952), in which the potassium was determined by flame photometry.

7. Results

In Table 1 we show the results obtained. In column 6 the figures have been corrected for the argon blank, and the volumes of radiogenic ^{40}A in column 9 have been calculated, using ^{36}A corrections. In the column headed "Days" is recorded the number of days which elapsed between grinding the sample and the analysis.

Taking the potassium branching ratio as 0·125 and λ as $5{\cdot}4 \times 10^{-10}$ year^{-1} (Gerling and Pavlova, 1951), the ages* obtained for the specimens are:—

Akaba	$3{\cdot}8 \times 10^9$ years
Brenham Township	$3{\cdot}5 \times 10^9$ years
Monze	$\leqq 1{\cdot}9 \times 10^9$ years
Granite	$4{\cdot}9 \times 10^8$ years

8. Discussion

The ages since solidification of the stone phases of the three meteorites are of the same order of magnitude as the age of the oldest rocks on the earth. Our results are to be compared with those of Gerling and Pavlova (1951), who found ages

* Note added in proof.

of $3{\cdot}03 \times 10^9$ years and $3{\cdot}00 \times 10^9$ years for the meteorites Zhovtnevy Khutor, and Saratov, respectively. Festa and Santangelo (1950), from calculations based on the decay ^{40}K—^{40}Ca also concluded that the silicate meteorites are probably $3{\cdot}6 \times 10^9$ years old.

Table 1

Sample	*No.*	*Method*	*Weight in g*	*Total vol. A obtained cc s.t.p.*	*A/g (less blank) in* 10^{-5}*cc*	*Days*	^{36}A,%	*Radiogenic* ^{40}A *cc/g*
Granite	1	Flux	4·453	$7{\cdot}07 \times 10^{-4}$	14·6	2	0·034	$1{\cdot}43 \times 10^{-4}$
Granite	2	Heating	3·393	$4{\cdot}47 \times 10^{-4}$	12·2	360	0·060	$1{\cdot}09 \times 10^{-4}$
Granite	3	Flux	2·196	$2{\cdot}96 \times 10^{-4}$	10·9	1	0·094	$0{\cdot}99 \times 10^{-4}$*
Akaba	4	Flux	3·080	$2{\cdot}30 \times 10^{-4}$	5·64	1	0·094	$5{\cdot}49 \times 10^{-5}$
Akaba	5	Heating	5·224	$3{\cdot}18 \times 10^{-4}$	5·42	0	0·058	$5{\cdot}10 \times 10^{-5}$
Akaba	6	Heating	5·044	$3{\cdot}81 \times 10^{-4}$	6·88	360	0·063	$6{\cdot}21 \times 10^{-5}$*
BrenhamTownship	7	Flux	3·172	$1{\cdot}17 \times 10^{-4}$	1·93	1	0·273	$8{\cdot}4 \times 10^{-6}$*
BrenhamTownship	8	Flux	3·838	$2{\cdot}31 \times 10^{-4}$	4·56	20	0·307	$7{\cdot}8 \times 10^{-6}$*
Monze	9	Heating	3·085	$8{\cdot}54 \times 10^{-5}$	1·63	210		
Air	10						0·348	
Air	11						0·352	

Blanks			K content		
	Flux Method	$0{\cdot}56 \times 10^{-4}$ cc A		Granite	5·04%
	Heating Method	$0{\cdot}35 \times 10^{-4}$ cc A		Akaba	0·104%
				Brenham Township	0·019%
				Monze	0·119%

* Corrected for hydrocarbon contamination.

Of particular interest is our age for the olivine inclusions in the iron of the pallasite, Brenham Township. The maximum age of the metal is thought to be $2{\cdot}8 \times 10^8$ years (Dalton and Reasbeck, 1954), a value in agreement with the maximum age of some other iron meteorites (Dalton *et al.*, 1953). The inference is that the stone phase is about ten times older than the metal phase. Chackett *et al.* (1953) have already reported from uranium, thorium, and helium measurements that the stone phase in the Beddgelert meteorite is probably ten times older than the iron phase.

The conclusion to be drawn from this is that the stone has been embedded in molten iron late in its life, perhaps at the time of the catastrophe which gave birth to the meteorites. This conception of pallasite formation is compatible with the geological evidence (see, e.g., Lord Rayleigh, 1944), that the olivine fragments will not melt at the temperature of molten iron, which appears to have flowed round them. One must then explain the retention of the rare gases in the silicates during pallasite formation. No information is available on the partition of argon between

stone and iron in such circumstances; but if the iron cooled rapidly there might be little "degassing" of the stone.

The discrepancy between the ages of the stone and iron may arise from other causes, such as production of argon or helium in the stone meteorites by cosmic rays, or loss of helium from the iron meteorites. If argon had been produced in the stone meteorites by cosmic-ray-induced spallation processes, then substantial amounts of ^{36}A and ^{38}A should have been present also. We have found no evidence for the presence of significant amounts of these isotopes. We have, however, found some small variation in the $^{36}A/^{38}A$ ratio, which we intend to investigate.

We think it unlikely that helium is lost from the iron meteorites by diffusion. Previously a very careful study of the helium concentration in Carbo meteorite (Paneth, Reasbeck, and Mayne, 1953), indicated an increase in concentration near the surface, whereas losses by diffusion would lead to a concentration gradient in the opposite sense; this confirms the work of Paneth (1939), who suggests that helium can only escape from iron to an appreciable extent if it is molten. Diffusion studies on the lines of those conducted by Jost and Widmann (1935) would be desirable.

The foliated granite came from an area in South Harris which is believed to be Precambrian. Strong thrusting movements in this region have resulted in a change in the granite and a probable loss of argon. The geology of the area has been discussed by Jehu and Craig (1927). We propose to continue this work on better defined granites.

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Note Added in Proof

After finishing our work, Professor F. A. Paneth kindly informed us of a communication received by him from G. J. Wasserburg and R. J. Hayden, in which they reported ages of about $4{\cdot}6 \times 10^9$ years for three meteorites. Using their value for the ^{40}K potassium branching ratio, viz., 0·085, we have calculated that the ages of our specimens would be: Akaba, $4{\cdot}4 \times 10^9$; Brenham Township (Stone), $4{\cdot}0 \times 10^9$; Monze, $2{\cdot}3 \times 10^9$; Granite, $6{\cdot}6 \times 10^8$ years.

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Some basaltic provinces

Jack Green[1] and Arie Poldervaart[2]

ABSTRACT

Areal averages are computed for basalts from the Pacific (12 areas, 116 analyses) and the Atlantic (9 areas, 25 analyses). Also tabulated are 31 averages of Cenozoic, 12 of Mesozoic, 6 of Paleozoic, and 8 of Precambrian basaltic provinces throughout the world. It is concluded that (1) the bulk of oceanic basalts are silica-undersaturated, (2) there is no consistent variation in the composition of basalt magma with time, and (3) there are no distinct types of basalt magma, but rather a continuous series from silica-saturated (tholeiitic) to silica-undersaturated (olivine-basaltic) rocks. This seems in accord with the theory that basaltic magma is formed by partial melting of the upper mantle.

Realization of the distribution on the surface of the earth of relatively thick shields of silicic continental rocks, separated by large oceanic shields with a relatively thin basaltic crust, has focused attention on the petrogenesis of basalt. This necessitates knowledge of the chemical composition of basalt. Kennedy and Anderson (1938) have suggested that there are two distinct types of basalt; olivine basalt and tholeiite. Others think that there may be chemical differences in basalts of different ages and different provinces. To test these ideas the authors have compiled averages for several of the better-known basaltic provinces of the world. These data are presented in the following tables.

Tables 1 and 3 give averages for various areas in the Pacific and Atlantic oceans. Analyses of rocks from these regions were screened, using the following percentage ranges: SiO_2 41·0–51·0, TiO_2 0·5–5·0, Al_2O_3 11·5–19·0, Fe_2O_3 0·5–10·0, FeO 0·5–13·0, MnO 0·0–1·0, MgO 4·5–12·0, CaO 7·0–16·0, Na_2O 1·4–4·0, K_2O 0·1–2·0, H_2O^+ 0·0–3·5, total $H_2O < 5·0$, P_2O_5 0·0–1·3, other constituents $< 2·0$, total 99·0–100·9. For the Pacific, exclusive of the Hawaiian Archipelago, 63 out of 262 analyses passed the screen. A breakdown of the 199 rejected analyses is given in Table 2. Only 26 rejected analysis are basalts as named by the authors. For the Hawaiian Islands the average of 53 analyses computed by Macdonald (1949) was used. For the central and southern Atlantic ocean only 25 analyses passed the screen.

Analyses which passed the screen were readily grouped into areas; 12 for the Pacific, and 9 for the Atlantic. Individual analyses were recalculated to 100 per cent minus H_2O^- and the average computed for each area. The gross average for each ocean was finally calculated from the area averages. Standard deviations for the anhydrous gross averages were calculated from the formula s: $\sqrt{\frac{\Sigma(M-m)^2}{n-1}}$, in which s: standard deviation, M: gross average, m: average for each area, and n: number of areas.

Table 4 gives 31 averages of Cenozoic, 12 of Mesozoic, 6 of Paleozoic, and 8 of Precambrian basaltic provinces, and also includes various type compositions. Analyses for these averages were again screened, but the SiO_2 range of the screen was increased to 55·0, K_2O to 2·5, and the MgO range was lowered to 2·5 per cent, to include some typical tholeiitic provinces. H_2O^+ was omitted from the screen, as averages were recalculated anhydrous. Other percentage ranges of the screen were the same as used for Tables 1 and 3. Overall averages were computed for the

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four groups from the averages listed, but for these the Pacific screen was again used and thus averages of tholeiitic provinces were excluded.

The close agreement between the Pacific and Atlantic gross averages is remarkable. Greater reliance may be placed on the Pacific average because of the larger number and spread of the analyses. The Pacific gross average, computed from the 12 area averages, does not emphasize the average for the Hawaiian Islands. Powers (1954) has noted that most analyses of Hawaiian basalts are of younger flows undersaturated in silica, while there are comparatively few analyses of older, silica-saturated basalts, believed to be volumetrically more prominent. The present data do not support the idea of the bulk of oceanic basalts being silica-saturated.

Averages listed in Table 4 do not indicate a consistent variation in the composition of basalt magma with time, nor do they support the view that there are distinct types of basalt magma. Instead there seems to be a continuous series from silica-saturated to silica-undersaturated basalts, some high in alumina, others of normal or low alumina content. Type compositions of olivine basalt and tholeiite are a matter of definition and application of suitable chemical screens. This only serves to emphasize a dominant characteristic of a basaltic province. However, in the opinion of the authors it would be unwise to overemphasize this definition and to infer that, for instance, there can be no synchronous olivine basalts in a tholeiitic province, or vice versa. The Karroo province of southern Africa is an example of a tholeiitic province in which one may observe all gradations between typical tholeiites and typical olivine basalts, e.g., in the Drakensberg, Transkei, Lebombo, Kaokoveld, and the remarkable volcanic complexes inland from Cape Cross.

Probably one may state that in the continental shields tholeiites are more common than in the oceanic shields, but this does not imply that there are no olivine basalts on the continents, nor that there are no tholeiites in the oceanic crust. Perhaps it may also be stated that active margins of oceanic shields are characterized by basalts high in alumina, as much as they seem to be marked by andesites (also high in alumina). More data than can be given here are needed to test this possibility, but again it does not necessarily follow that basalts high in alumina, or andesites, are found *only* in active margins of oceanic shields.

The main problem still remains: What causes basalt magmas to vary in place and time? Suggestions have been offered that this variation may result from contamination, mixing of magmas, or crystallization differentiation. Another possibility takes into account that heat and vapours with variable amounts of "dissolved" elements may ascend, perhaps differentially, from the interior parts of the earth, and collected along major fissures in the upper portions of the mantle, may partially melt the ultramafic sima. This process is implied in the "degassing" of the earth's interior. Not only does it seem possible that the upper mantle is not homogeneous, but the basaltic products of partial melting are also likely to differ according to the action of heat and different concentrations of vapours, with different amounts of dissolved elements. Variations in compositions of basalt magma in one province, and from one province to the next, may be more adequately interpreted in terms of this last process than by overemphasizing somewhat arbitrarily defined "primitive" basaltic types.

Table 1. *Pacific basalt averages*

Area	1	2	3	4	5	6	7	8	9	10	11	12	*Gross average*	*Anhydrous*	*Standard deviations*
SiO_2	46.62	47.61	47.44	46.96	45.14	45.92	43.18	47.05	48.35	45.24	47.08	48.15	46.57	47.0	1.5
TiO_2	3.47	2.35	4.03	2.46	3.67	3.62	3.76	2.42	2.77	2.75	2.16	2.06	2.96	3.0	0.7
Al_2O_3	15.41	16.68	14.80	14.76	16.75	15.87	13.41	13.27	13.18	14.91	14.63	15.53	14.93	15.1	1.2
Fe_2O_3	4.57	2.31	4.52	3.68	4.20	2.29	5.73	2.67	2.35	4.86	2.79	4.17	3.68	3.7	1.2
FeO	7.66	8.80	8.31	7.68	7.39	8.99	7.35	8.76	9.08	7.72	8.00	7.15	8.07	8.1	0.6
MnO	0.19	0.22	0.12	0.16	0.20	0.20	0.16	0.15	0.14	0.25	0.14	0.13	0.17	0.17	—
MgO	6.73	6.89	4.98	8.12	6.98	7.11	8.61	10.63	9.72	8.24	9.36	6.69	7.84	7.9	1.6
CaO	10.49	11.26	9.53	11.94	9.83	9.55	12.32	9.99	10.34	11.46	11.01	11.43	10.76	10.9	1.0
Na_2O	2.98	2.66	3.22	2.31	2.61	3.23	2.84	2.63	2.42	2.52	2.33	2.25	2.67	2.7	0.4
K_2O	0.96	0.51	0.88	0.65	1.53	1.28	1.40	1.37	0.58	1.06	0.93	1.04	1.02	1.0	0.3
H_2O^+	0.61	0.43	1.83	1.05	1.09	1.23	0.77	0.69	0.73	0.60	1.26	1.16	0.95	—	—
P_2O_5	0.30	0.26	0.34	0.22	0.42	0.70	0.40	0.33	0.34	0.19	0.31	0.23	0.34	0.34	0.1
Other	—	—	0.01	—	0.18	—	0.07	0.04	—	0.21	—	0.01	0.04	—	—

INDEX TO TABLE 1

Area 1—Juan Fernandez: 33.5° S, 80.8° W.
Average 3 analyses; Lacroix, 1927.

Area 2—Galapagos: *ca.* 0.5° S, 91° W.
Average 6 analyses; Lacroix, 1927; Richardson, 1933.

Area 3—Easter Island: 27.1° S, 109.3° W.
Average 6 analyses; Lacroix, 1939b.

Area 4—Gambier: *ca.* 23.2° S, 135.0° W.
Average 5 analyses; Lacroix, 1927.

Area 5—Marquesas: *ca.* 9° S, 140° W.
Average 9 analyses; Lacroix, 1927; Chubb, 1930.

Area 6—Rapa: 27.6° S, 144.4° W.
Average 3 analyses; Lacroix, 1927.

Area 7—Tahiti, Tubai Manu: 17.5° S, 149.5° W.
Average 10 analyses; Lacroix, 1927.

Area 8—Bora-bora, Tahaa, Huahiné: *ca.* 16.6° S, 151.5° W.
Average 4 analyses; Lacroix, 1927.

Area 9 Hawaiian Islands: 18 29° N, 155°–161° W.
Average 53 analyses; Macdonald, 1949.

Area 10 Futuna, Upolu: 13.6°–14.2° S, 172.0°–178.2° W.
Average 4 analyses; Lacroix, 1927, 1941.

Area 11—Aneityum (Anatom), Maré (Peorawa), Uvéa: 20.0°–21.8° S, 166.5°–170.0° E.
Average 4 analyses; Lacroix, 1941.

Area 12 Eromanga (Erromango), Efate (Vate), Vanikoro (Manevai), Pentecôte, Tikopia, Aoba: 11.5° 18.4° S; 167°–169° E.
Average 9 analyses; Lacroix, 1941.

Table 2. Rejected 199 Pacific analyses

SiO_2	TiO_2	Al_2O_3	Fe_2O	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O^+	H_2O *tot.*	CO_2	*No. anal.*	*No. basalts*	*Tot. No. anal.*
> 55				< 2.0								70	—	70
51–55												5	1	
				≷ 4.5								6	—	
		> 19.0		< 4.5								2	—	
		> 19.0		< 4.5			> 2.0					1	—	
		> 19.0		< 4.5	< 7.0	> 4.0	> 2.0					2	—	
		> 19.0			< 7.0	> 4.0	> 2.0					1	—	
			< 0.5	< 4.5								1	—	
				< 4.5		> 4.0						1	1	
				< 4.5		> 4.0	> 2.0					2	—	
				< 4.5	< 7.0	> 4.0	> 2.0					5	—	
							> 2.0					1	1	27
< 41												1	—	
	> 5.0											1	—	
	> 5.0						> 2.0	> 1.3				1	—	
		< 11.5		> 12.0		< 1.4						1	—	
			> 10.0	< 4.5	< 7.0				> 3.5	> 5.0		1	—	
				< 4.5						> 5.0		1	—	
					> 16.0	< 1.4						1	—	
						> 4.0	> 2.0					1	—	
									> 3.5	> 5.0		1	—	9
41–51	> 5.0											4	1	4
41–51		> 19.0										2	—	
		> 19.0		< 4.5		> 4.0	> 2.0					2	—	
		> 19.0		< 4.5	< 7.0	> 4.0	> 2.0					5	—	
		> 19.0		< 4.5	< 7.0	> 4.0	> 2.0				> 2.0	1	—	10

41–51		< 11.5									1	1		
	> 5.0	< 11.5									1	1		
	> 5.0	< 11.5		> 12.0							1	—		
		< 11.5		> 12.0							11	5		
		< 11.5	> 10.0	> 12.0							1	—		
		< 11.5		> 12.0	< 7.0	< 1.4					3	—		
		< 11.5		> 12.0		< 1.4					7	1		
		< 11.5		> 12.0		< 1.4			> 3.5		1	—		
		< 11.5		> 12.0			< 0.1				1	—	27	
41-51			> 10.0				> 2.0				1	—	1	
41–51				> 12.0							1	—		
				> 12.0		> 4.0					4	1		
				> 12.0		< 1.4					1	1	6	
41–51				< 4.5							12	5		
				< 4.5	< 7.0	> 4.0					1	—		
				< 4.5	< 7.0	> 4.0	> 2.0				8	—		
				< 4.5	< 7.0	> 4.0	> 2.0		> 3.5		2	—		
				< 4.5	< 7.0				> 3.5	> 5.0	1	—		
				< 4.5		> 4.0	> 2.0				4	—		
				< 4.5		> 4.0	> 2.0		> 3.5		1	—		
				< 4.5			> 2.0				2	2	31	
41–51						> 4.0					5	1		
	> 5.0					> 4.0	> 2.0				1	—	6	
41–51							> 2.0				3	2		
								> 1.3			1	—		
								n.d.	n.d.	n.d.	1	1		
										> 2.0	1	1	4	
	Phosphate rocks										2	—	2	

Table 3. Atlantic basalt averages

Area	1	2	3	4	5	6	7	8	9	*Gross average*	*Anhydrous*	*Standard deviations*
SiO_2	48.42	44.01	48.99	49.48	47.56	43.28	44.13	46.51	45.66	46.45	46.9	2.3
TiO_2	2.91	0.82	3.38	0.78	3.12	3.51	2.83	3.63	2.86	2.65	2.7	1.1
Al_2O_3	13.88	17.44	14.43	16.45	15.69	13.67	14.70	12.96	14.33	14.84	15.0	1.4
Fe_2O_3	6.39	7.26	1.04	2.30	3.71	2.75	4.65	5.70	6.20	4.44	4.5	2.1
FeO	5.90	6.07	8.57	7.54	8.72	10.24	8.68	6.19	6.74	7.63	7.7	1.5
MnO	0.11	—	0.24	0.19	0.17	0.16	—	0.11	0.27	0.14	0.14	—
MgO	7.57	6.05	7.51	7.90	5.98	10.18	8.58	7.52	8.26	7.73	7.8	1.3
CaO	9.40	12.08	8.91	11.42	9.41	10.56	10.60	12.05	10.89	10.59	10.7	1.2
Na_2O	2.30	3.42	3.57	2.62	3.19	3.04	2.93	2.68	2.53	2.92	2.9	0.4
K_2O	1.64	1.58	1.78	0.30	0.93	1.33	1.24	1.10	0.89	1.20	1.2	0.5
H_2O+	0.96	0.96	0.95	0.95	0.94	0.95	0.96	0.95	0.94	0.95	—	–
P_2O_5	0.53	0.32	0.63	0.08	0.61	0.33	0.72	0.60	0.45	0.48	0.48	0.2

INDEX TO TABLE 3

Area 1—Fernando Po: *ca.* 3° N, 10° E.
One analysis; BOESE, 1912.
Area 2—St. Helena: *ca.* 17° S, 7° W.
One analysis; REINISCH, 1912.
Area 3—Gough Island: *ca.* 40° S, 10° W.
One analysis; SMITH, 1930.
Area 4—dredged block: 1.9° S, 12.7° W.
One analysis; CORRENS, 1930.
Area 5—Ascension: 8.0° S, 14.9° W.
Average 2 analyses; DALY, 1925.
Area 6—Canary Islands: *ca.* 28° N, 16° W.
Average 2 analyses; BOURCART and JÉRÉMINE, 1938; PREISWERK, 1909.
Area 7—Madeira: *ca.* 33° N, 17° W.
Average 12 analyses; GAGEL, 1912.
Area 8—Cape Verde: *ca.* 17° N, 23° W.
One analysis; BACELAR, 1932.
Area 9—Azores: *ca.* 38° N, 25° W.
Average 4 analyses; ESENWEIN, 1929; VON JOHN, 1896.

Table 4. World basalt averages

Index	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
No. analyses	2	11	8	7	5	4	8	14	2	3	—	7	6	—	24
SiO_2	49.1	51.5	46.9	47.4	48.4	46.5	49.2	48.0	48.2	47.1	46.9	48.4	50.6	47.0	47.7
TiO_2	1.9	1.6	2.4	2.2	2.8	3.4	1.9	2.9	1.4	2.9	2.7	0.9	3.0	3.0	2.3
Al_2O_3	14.1	14.3	15.4	15.6	16.1	16.2	14.1	12.9	19.1	14.0	15.0	19.2	13.9	15.1	15.8
Fe_2O_3	4.7	3.5	3.9	3.7	3.2	3.3	3.4	4.3	1.2	4.9	4.5	1.8	2.4	3.7	5.3
FeO	9.3	9.2	9.8	9.2	8.6	7.9	9.9	9.1	8.7	8.0	7.7	7.3	11.8	8.1	8.8
MnO	0.3	0.3	0.3	0.3	0.2	0.3	0.3	0.2	0.1	0.2	0.1	0.1	0.2	0.2	0.2
MgO	6.2	5.3	8.4	8.5	6.3	6.0	6.7	7.7	7.9	7.2	7.8	8.0	4.7	7.9	4.7
CaO	11.3	10.1	9.6	10.2	11.2	10.4	11.8	11.4	10.7	13.0	10.7	11.2	8.3	10.9	9.9
Na_2O	2.5	2.8	2.5	2.1	2.5	3.2	2.0	2.4	2.4	1.7	2.9	2.7	3.0	2.7	3.4
K_2O	0.4	1.1	0.6	0.6	0.5	2.2	0.5	0.7	0.2	0.7	1.2	0.3	1.3	1.0	1.5
P_2O_5	0.2	0.3	0.2	0.2	0.2	0.6	0.2	0.4	0.1	0.3	0.5	0.1	0.8	0.3	0.4

Cenozoic rocks

1. Franz Josef Land; Washington, 1922.
2. Nonporphyritic central basalts, Scotland; Walker and Poldervaart, 1949.
3. Plateau basalts, Scotland; Bailey *et al.*, 1924.
4. Hebrides; Walker and Poldervaart, 1949.
5. Faroes; Walker and Davidson, 1936.
6. Jan Mayen; Tyrrel, 1926
7. Iceland; Tryggvason, 1943.
8. East Greenland; Backlund and Malmqvist, 1932; Wager, 1934; Wager and Deer, 1939; Krokström, 1944.
9. Skaergaard intrusion, East Greenland; Wager and Deer, 1939.
10. West Greenland; Noe-Nygaard, 1942.
11. Atlantic; this paper.
12. Medicine Lake, California, U.S.A.; Powers, 1932; Anderson, 1941.
13. Oregon, U.S.A.; Walker and Poldervaart, 1949.
14. Pacific; this paper.
15. Eastern Otago, New Zealand; Benson, 1941; 1944.

Table 4 (continued)

Index	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
No. analyses	14	14	3	10	25	6	3	12	50	36	16	4	5	14	29	24	—
SiO_2	49.0	49.1	52.5	48.5	48.6	48.5	51.1	48.7	49.0	49.4	50.4	48.3	48.0	46.2	48.2	47.6	48.2
TiO_2	3.2	0.9	0.9	1.9	1.8	2.0	1.0	1.4	2.3	1.2	0.9	2.4	1.3	3.0	2.9	2.4	2.3
Al_2O_3	15.7	15.6	16.0	15.1	15.5	13.8	15.0	16.6	16.5	19.2	18.9	17.1	16.0	14.7	14.1	15.0	15.3
Fe_2O_3	3.6	5.4	2.8	3.1	4.1	6.5	3.4	4.2	4.0	3.8	3.3	4.2	5.6	3.3	2.6	3.7	4.1
FeO	8.1	6.4	6.5	8.7	7.7	6.8	8.4	6.5	6.8	6.5	7.5	6.9	7.5	9.5	9.1	8.0	8.3
MnO	0.2	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	—	0.2
MgO	6.0	7.7	7.1	9.2	8.3	7.2	6.1	7.6	5.6	5.2	5.4	6.6	7.4	8.5	7.7	7.5	7.1
CaO	8.4	10.2	11.0	9.1	8.9	9.4	11.1	11.2	9.3	10.4	11.0	9.2	9.9	10.6	11.8	12.0	10.4
Na_2O	3.7	3.1	2.4	2.8	3.0	3.2	3.0	2.6	3.6	2.8	2.0	3.2	3.0	2.8	2.3	2.7	2.7
K_2O	1.4	1.0	0.5	1.1	1.4	1.7	0.6	0.7	2.0	0.9	0.3	1.6	0.9	0.9	0.9	0.8	1.0
P_2O_5	0.7	0.4	0.1	0.4	0.5	0.7	0.1	0.3	0.7	0.4	0.1	0.3	0.2	0.3	0.3	0.3	0.4

Cenozoic rocks (continued)

16. Banks Peninsula, New Zealand; Benson, 1941.
17. Tertiary, Auckland, New Zealand; Benson, 1941.
18. Quaternary, Auckland, New Zealand; Benson, 1941.
19. Tasmania; Edwards, 1950.
20. Tertiary, Victoria, Australia; Edwards, 1938c; 1939.
21. Quaternary, Victoria, Australia; Edwards and Crawford, 1940.
22. Western Australia; Edwards, 1938a
23. Indonesia; Willems, 1940.
24. Eastern Asia; Tomita, 1935.
25. Japan; Iwasaki, 1937.
26. Huzi volcanic zone, Japan; Tsuya, 1937.
27. Morotu, Sakhalin; Yagi, 1953.
28. Kerguelen Archipelago; Edwards, 1938b.
29. Mauritius; Walker and Nicolaysen, 1954.
30. Reunion; Lacroix, 1936; 1939a.
31. Madagascar; Lacroix, 1923.
32. Average Cenozoic basaltic rocks (screened).

Table 4 (continued)

Index	33	34	35	36	37	38	39	40	41	42	43	44	45
No. analyses	4	4	4	8	8	6	9	16	2	17	43	5	—
SiO_2	50.0	49.5	52.2	52.1	51.6	53.3	47.4	51.3	54.0	49.8	52.5	52.2	49.2
TiO_2	2.9	1.5	1.3	1.3	2.0	0.6	2.4	1.9	0.7	1.7	1.0	1.0	2.1
Al_2O_3	14.7	14.1	15.4	14.7	13.5	16.4	14.6	14.0	16.1	15.0	15.4	15.6	14.6
Fe_2O_3	3.4	4.8	1.6	3.4	5.3	0.5	4.6	3.3	0.8	2.7	1.2	2.7	3.9
FeO	10.3	10.1	8.7	8.6	7.7	8.3	7.3	10.1	7.4	10.2	9.3	7.9	9.5
MnO	0.4	0.2	0.1	0.1	0.2	0.2	0.2	0.3	0.1	0.2	0.2	0.2	0.2
MgO	5.5	6.1	7.3	7.0	6.3	6.7	8.0	5.5	7.0	6.5	7.1	7.2	6.5
CaO	9.6	9.9	10.0	8.9	9.8	11.5	9.9	9.8	11.1	10.9	10.3	10.1	10.1
Na_2O	2.0	2.7	2.4	3.0	2.4	1.6	3.4	2.8	1.8	2.2	2.1	2.0	2.6
K_2O	1.0	0.7	0.8	0.7	1.0	0.9	1.7	0.7	1.0	0.6	0.8	0.9	1.0
P_2O_5	0.2	0.4	0.2	0.2	0.2	—	0.5	0.3	—	0.2	0.1	0.2	0.3

Mesozoic rocks

33. Intrusives, Spitsbergen; TYRRELL and SANFORD, 1933.
34. Extrusives, Spitsbergen; TYRRELL and SANFORD, 1933.
35. Palisade intrusion, U.S.A.; WALKER and POLDERVAART, 1949.
36. Watchung extrusives, U.S.A.; WALKER and POLDERVAART, 1949.
37. South America; WALKER and POLDERVAART, 1949.
38. Tasmania; EDWARDS, 1942.
39. Eastern China; LACROIX, 1928.
40. Deccan, India; TYRRELL and SANDFORD, 1933.
41. Antarctica; WALKER and POLDERVAART, 1949.
42. Siberia; WALKER and POLDERVAART, 1949.
43. Karroo intrusives, South Africa; WALKER and POLDERVAART, 1949.
44. Karroo extrusives, South Africa; WALKER and POLDERVAART, 1949.
45. Average Mesozoic basaltic rocks (screened).

Table 4 (continued)

Index	46	47	48	49	50	51	52
No. analyses	21	32	27	6	7	32	—
SiO_2	50.2	51.6	47.0	49.1	53.4	49.5	49.0
TiO_2	2.8	2.7	2.9	3.2	1.3	1.8	2.7
Al_2O_3	15.4	15.0	15.7	13.9	15.0	15.4	15.1
Fe_2O_3	4.3	3.4	4.1	4.0	4.0	3.0	3.9
FeO	8.2	9.6	8.4	11.0	7.9	9.3	9.2
MnO	0.2	0.2	0.2	0.3	0.2	0.2	0.2
MgO	5.1	4.9	7.4	5.3	5.2	7.0	6.2
CaO	8.1	8.9	9.4	8.7	7.8	9.9	9.0
Na_2O	3.5	2.4	3.1	3.0	2.9	2.4	3.0
K_2O	1.7	1.1	1.3	1.1	2.0	1.1	1.3
P_2O_5	0.5	0.2	0.5	0.4	0.3	0.4	0.4

Paleozoic rocks

46. Southern Sweden and Norway; GJELSVIK, 1952; BRØGGER, 1933; LARSSON, 1932.
47. Northern England and Scotland; WALKER and POLDERVAART, 1949.
48. Scotland; TOMKEIEFF, 1937.
49. Roan Mountain district, North Carolina, U.S.A.; unpublished data, WILCOX and POLDERVAART.
50. East Kimberley, Western Australia; EDWARDS and CLARKE, 1940.
51. Cape Folded Belt intrusives, South Africa; NELL and BRINK, 1945; POTGIETER, 1950; BOUMAN, 1950.
52. Average Paleozoic basaltic rocks (screened).

Table 4 (continued)

Index	53	54	55	56	57	58	59	60	61
No. analyses	10	21	17	9	10	—	4	17	—
SiO_2	49.8	48.5	47.1	48.0	49.0	50.9	49.9	52.0	49.1
TiO_2	1.1	2.2	2.1	1.5	1.5	0.5	1.2	0.8	1.4
Al_2O_3	17.6	16.1	17.1	17.6	17.5	17.7	15.5	15.5	17.0
Fe_2O_3	1.9	3.2	2.9	1.9	3.4	0.3	3.3	1.9	2.4
FeO	7.7	10.9	10.7	9.3	8.0	10.0	10.0	8.0	9.5
MnO	0.2	0.2	0.1	0.2	0.2	0.2	0.3	0.2	0.2
MgO	6.8	5.8	6.9	8.1	6.7	7.7	6.0	8.5	6.9
CaO	11.6	8.4	9.2	9.6	10.2	10.5	10.7	10.6	10.0
Na_2O	2.2	3.0	2.8	2.9	2.8	1.9	2.4	1.8	2.6
K_2O	0.7	1.1	0.8	0.7	0.5	0.2	0.5	0.6	0.6
P_2O_5	0.4	0.6	0.3	0.2	0.2	0.1	0.2	0.1	0.3

Precambrian rocks

53. Southwestern Finland; SIMONEN, 1948.
54. Norway and Sweden; KROKSTRÖM, 1932; 1936; VON ECKERMANN, 1936; 1939; GJELSVIK, 1952.
55. Southern Norway; BRØGGER, 1935; GJELSVIK, 1952.
56. Adirondacks, U.S.A.; BUDDINGTON, 1952.
57. Keweenawan, U.S.A.; CORNWALL, 1951.
58. Stillwater complex, U.S.A.; HESS (personal communication).
59. Waterberg lavas, South Africa; VAN ZYL, 1950.
60. Bushveld complex, South Africa; HALL, 1938.
61. Average Precambrian basaltic rocks (screened).

Table 4 (continued)

Index	62	63	64	65	66	67
No. analyses	198	43	96	—	137	—
SiO_2	49.9	49.7	46.1	47.0	51.3	51.0
TiO_2	1.4	2.2	2.6	3.0	2.0	1.4
Al_2O_3	16.0	14.2	14.8	15.1	14.2	15.6
Fe_2O_3	5.4	3.7	3.2	3.7	2.9	1.1
FeO	6.5	10.0	8.8	8.1	9.1	9.8
MnO	0.3	0.2	0.2	0.2	0.2	0.2
MgO	6.3	6.8	9.4	7.9	6.4	7.0
CaO	9.1	9.6	10.8	10.9	10.5	10.5
Na_2O	3.2	2.6	2.7	2.7	2.3	2.2
K_2O	1.5	0.7	1.0	1.0	0.9	1.0
P_2O_5	0.4	0.3	0.4	0.3	0.2	0.2

Basaltic averages

62. All basalts; DALY, 1933.
63. Plateau basalts; DALY, 1933.
64. Alkali basalts; NOCKOLDS, 1954.
65. Pacific olivine basalts; this paper.
66. Tholeiites; NOCKOLDS, 1954.
67. Tholeiites; this paper.

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The principles governing trace element distribution during magmatic crystallization

Part I: The influence of electronegativity

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ABSTRACT

The Goldschmidt Rules dealing with the distribution of trace elements in magmatic minerals require modification to allow for the differing electronegativities of elements which display diadochy. If the trace element possesses a substantially higher electronegativity than the element which camouflages it, it will tend to form more covalent, and consequently weaker bonds in the crystal than its host. Such an element will not be accepted readily into the crystal and therefore becomes concentrated in residual magmas. If the electronegativity of the trace element is less than that of its host, the positions are reversed and it will be preferentially concentrated in crystals containing the host element. These relationships apply when the electronegativity difference between the host and the trace element is greater than 0·1 (approx.). When the difference is 0·1 or less, the original Goldschmidt Rules are usually valid.

1. Introduction

The principles governing trace element distribution in minerals were first formulated by Goldschmidt. Although his discovery that the behaviour of trace elements is governed by ionic radii rather than position in the periodic table, remains a fundamental law, there has been a widespread realization during recent years that the Goldschmidt (1937a) Rules of trace element distribution are very much in need of revision. Shaw (1953) has recently criticized the validity of these rules and listed numerous exceptions to them. Fyfe (1951) and Ramberg (1952) have also pointed out that they require modification in some respects.

In this contribution, an examination will be made of the fundamental principles controlling trace element distribution in an attempt to explain the discrepancies.

In Part I, consideration will be limited to the behaviour of univalent, divalent, and the larger trivalent ions. The smaller trivalent ions, together with ions possessing valencies greater than three will be dealt with in Part II. Justification for this division lies in the fundamentally different behaviour of the two groups which will be discussed also in Part II.

2. The Goldschmidt Rules

Goldschmidt (1937a) proposed a series of rules governing the mutual replacement (diadochy) of ions in magmatic minerals, on the assumption that the bonding in those minerals was purely ionic. He considered that when two ions are able to substitute for one another in a crystal structure the ion which makes the larger contribution to the energy of the structure is preferentially incorporated. These considerations gave rise to three rules. The first rule is derived from observation whilst the second and third are consequences of the inverse square law of electrostatic attraction applied to ionic lattices.

(i) For two ions to be able to replace one another in a crystal structure the ionic radii must not differ by more than 15 per cent.

(ii) When two ions which possess the same charge but different radii compete for a lattice site, the ion with the smaller radius is preferentially incorporated.

(iii) When two ions possessing similar radii but different charges compete for a lattice site, the ion with the higher charge is preferentially incorporated.

These rules are found to account adequately for the behaviour of a few trace elements in the magma but they break down rather frequently (Shaw, 1953). The principal reason for this breakdown is that Goldschmidt did not adequately take into account the influence of the partial covalent bonding which coexists with ionic bonding in the lattices under consideration.

This influence will be considered in detail in the following pages.

3. Chemical Bonding

During recent years the importance of the type of chemical bonding in geochemical problems has been receiving increasing recognition. Neumann (1949) and Fyfe (1951) have pointed out with special reference to zinc compounds that the directional properties of partial covalent bonds may affect in some cases the laws governing isomorphism, whilst Ramberg (1952) utilized bond-type concepts in explaining the distribution of some major cations in silicates. Ahrens (1953) has attempted to interpret a wide range of geochemical phenomena in terms of chemical bonding. Some of his views will be dealt with subsequently.

The papers mentioned above are largely based upon applications of the fact that chemical bonds in the great majority of compounds are neither completely ionic nor completely covalent. They are nearly always of an intermediate nature. An admirable summary of the transitional nature of chemical bonds has been published recently by Ahrens (1953) but in the interests of continuity some repetition is necessary.

There are two principal types of chemical bonds—the ionic bond due to electrostatic attraction between oppositely charged ions, and the covalent bond, due to electron sharing between atoms. The bond between any two atoms or ions nearly always involves a combination of the two extreme types. The bond between two like atoms is essentially covalent. However, when one atom differs from the other, an ionic component is introduced. The property of the atoms which is concerned is the electronegativity, or "the power of an atom in a molecule to attract electrons to itself" to quote Pauling (1940). When two atoms of similar electronegativity are joined by a bond it will be covalent since both atoms tend to attract the bonding electrons to the same extent, and hence the electron distribution is symmetrical. If, however, one of the atoms has a higher electronegativity than the other it will draw the shared electrons closer towards itself. This means that the more electropositive atom becomes positively charged to some extent, whilst the electronegative atom becomes negatively charged. Thus an ionic component is introduced into the bond. The greater the difference in electronegativity between two atoms the more ionic will the bond become. By assigning the elements electronegativity values calculated from thermal data, Pauling (1940) has developed a method of calculating the amount of ionic or covalent character in any bond.

Ahrens (1953) and Goldschmidt (1954) have suggested the use of ionization

Table 1. *Melting temperatures and thermal behaviour of isostructural compounds containing noble and non-noble gas type cations*

Compound	*Radius of cation* Å	*Crystal structure*	*Electro-negativity*	*M.P.* °C
KF	1·33	NaCl	0·8	880
AgF	1·26	NaCl	1·8	435
KCl		NaCl		776
AgCl		NaCl		455
$KClO_4$		$NaClO_4$		610
$AgClO_4$		$NaClO_4$		486
Na_2SO_4	0·99	Na_2SO_4	0·9	884
Ag_2SO_4	1·26	Na_2SO_4	1·8	652
RbF	1·47	NaCl	0·8	760
TlF	1·47	Distorted NaCl	1·5	Boils, 300
RbCl		CsCl		715
TlCl		CsCl		430
Rb_2SO_4		K_2SO_4		1,060
Tl_2SO_4		K_2SO_4		632
CaO	0·99	NaCl	1·0	2,572
CdO	0·97	NaCl	1·5	d. 900
CaF_2		CaF_2		1,360
CdF_2		CaF_2		1,100
SrF_2	1·12	CaF_2	1·0	1,190
PbF_2	1·20	CaF_2	1·6	855
$SrSO_4$		$BaSO_4$		1,605
$PbSO_4$		$BaSO_4$		d. 1,000
$Sr(NO_3)_2$		$Ca(NO_3)_2$		570
$Pb(NO_3)_2$		$Ca(NO_3)_2$		d. 470
Y_2O_3	0·91	Tl_2O_3	1·2	2,410
In_2O_3	0·81	Tl_2O_3	1·6	d. 850
Y_2O_3	0·91	Tl_2O_3	1·2	2,410
Tl_2O_3	0·95	Tl_2O_3	1·9	717
SrF_2	1·12	CaF_2	1·0	1,190
HgF_2	1·10	CaF_3	1·9	570
CaO	0·99	NaCl	1·0	2,572
MnO	0·80	NaCl	1·4	1,650

Table 1 (*continued*)

Compound	*Radius of cation* Å	*Crystal structure*	*Electro-negativity*	*M.P.* °C
CaF_2	0·99	CaF_2	1·0	1,378
CuF_2	0·72	CaF_2	2·0	500
MgO	0·66	NaCl	1·2	2,800
NiO	0·69	NaCl	1·7	1,990
MgF_2		SnO_2		1,396
NiF_2		SnO_2		Subl. 1,000
MgO	0·66	NaCl	1·2	2,800
CaO	0·99	NaCl	1·0	2,572
CoO	0·72	NaCl	1·7	1,935
Al_2O_3	0·51	Cr_2O_3	1·5	2,050
Ga_2O_3	0·62	Cr_2O_3	1·6	1,740
AlN		ZnO		d. 2,200
GaN		ZnO		Sub. 1,800
TiO_2 (Rutile)	0·68	SnO_2	1·6	1,825
SnO_2	0·71	SnO_2	1·8	1,625
TiO_2 (Rutile)	0·68	SnO_2	1·6	1,825
RuO_2	0·67	SnO_2	2·05	d. 1,000
TiO_2 (Rutile)	0·68	SnO_2	1·6	1,825
TeO_2	0·70	SnO_2	2·1	733

N.B. Melting-point data were obtained from—
(1) *Handbook of Chem. and Phys.*, 13th Ed., 1948. Chem. Pub. Co.
(2) *Handbook of Physical Constants*, Geol. Soc. Am. Spec. Paper, No. 36, 1943.
(3) Mellor, J. W. *A Comprehensive Treatise of Inorganic and Theoretical Chemistry.* 16 vols. Longmans Green, 1922–37.
The values for ionic radii used in this paper are from the table given by Ahrens (1952).
Electronegativity values used in this paper are taken from Pauling (1940) and Haissinsky (1946).

potentials as a relative measure of the ionic or covalent character of the chemical bond. This usage which is based upon the polarization model of transitional chemical bonding (Fajans, 1943), also gives satisfactory results and could be used to replace the electronegativity criterion if so desired.

4. The Weakening Effect of Partial Covalent Bonding

This is best studied by comparing the properties of crystal structures in which cations possessing similar charges and radii but different electronegativities, are substituted for one another. Under these conditions the difference in the properties of the pairs of compounds is due essentially to the effect of increased covalent bonding in the compound containing the cation with the greater electronegativity.

This is so since the other parameters which determine crystal energy—namely ionic charge, ionic radius, and crystal structure, are kept constant. Table 1 contains a list of the melting points of pairs of compounds conforming to these conditions. The ions with the greater electronegativity are all derived from B sub-group or transition elements, the higher electronegativity being due to the non-noble gas electron configuration of these ions.

It will be noticed that in every case the compound containing the B sub-group or transition element possesses a lower melting temperature than its A sub-group counterpart, indicating weaker bonding. After a comparison of hardnesses and melting points of similar pairs of compounds, STILLWELL (1938) concluded: "Without exception the compounds of B cations are weaker in respect to both hardness and melting points than are the A cation compounds. . . . In short we are dealing with an intermediate covalent-ionic bond, which has all the attributes of a loosened or weakened bond." This conclusion has also been reached by AHRENS (1953).

Applied to trace element behaviour, these principles give rise to the following rule which is of widespread applicability.

Whenever diadochy in a crystal is possible between two elements possessing appreciably different electronegativities the element with the lower electronegativity will be preferentially incorporated because it forms a stronger and more ionic bond than the other.[1] In practice, this rule is found to apply to diadochic substitutions involving elements which differ in electronegativity by more than 0·1.

However, when diadochy occurs between elements possessing similar electronegativities the Goldschmidt Rules may be applied (although some exceptions occur). Thus, the smaller of the competing ions is usually preferentially incorporated in crystals provided the ionic charges are equal. Similarly, the more highly charged of the competing ions is preferentially enriched.

The rule stated previously may be established by an alternative line of argument which however is fundamentally similar. Where diadochy occurs between a trace element and a major element, the pair can be regarded as forming a limited solid solution series. This approach has been suggested by SHAW (1953). The compound with the higher melting point is always relatively enriched in the early high temperature crystals of a simple solid solution series. Therefore when diadochy occurs between an A sub-group element and a B sub-group or transition element, the early high temperature crystals will be relatively enriched in the A sub-group element, i.e., the element with the lower electronegativity. This follows, because when isostructural compounds of A and B sub-group elements possessing similar valencies are compared, those containing the former always possess higher melting points (Table 1).

It will be shown subsequently that the above rule based on electronegativities helps to determine the behaviour of the following trace elements:

Cu^{1} Ag^{1} Cu^{2} V^{3} Cr^{3} Sn^{2} Mn^{2} Ni^{2} Cd^{2} Pb^{2} Hg^{2} Sb^{3} Bi^{3} $Sc^{3}Zn^{2}$, and the rare earths.

[1] RANKAMA and SAHAMA (1950, p. 122) quote GOLDSCHMIDT as having pointed out that when extensive diadochy occurs between two ions, the ionization potentials are usually fairly similar. This implies that electronegativity is one factor governing diadochy, since electronegativity is a property closely related to ionization potential (PAULING, 1940). However, no interpretation is offered.

5. The "Field Function" Concept

Ahrens (1953) has recently attempted to explain some aspects of trace element behaviour in terms of a new concept—the "Field Function" or F value of an ion. For any ion, F is defined as I/R where I is the ionization potential and R is the ionic radius. F is therefore claimed to be a measure of the electric intensity of an ion. Ahrens states his principle thus:

"When two ions of the same valence and equal to similar radii compete for a given structure site in a growing crystal, the one with the greater electric intensity (field) should arrive first."

It is suggested that in certain cases, the ion which arrives first is preferentially incorporated in the crystal.

This concept is rather difficult to visualize precisely in atomistic terms; however assuming its applicability, the electric intensity which would be involved is the *external field strength* of the ion, given by Ze/R^2 where Ze is the ionic charge and R is the ionic radius. The F value (I/R) is only a measure of electric intensity when the electronic fields of the cation and anion are in contact and overlap—i.e., F valves are only significant when the cation has already taken its place in the lattice. Consequently F values cannot be used to indicate the order in which competing ions arrive at a lattice site.

Furthermore the rule breaks down rather frequently even in the limited field to which Ahrens restricts its application. Consider the following pairs of ions which possess similar radii and equal charges. The first of the pair is nearly always relatively enriched in the early crystallates from magmas.

Table 2

	F	
V^3	36	(1)
Fe^3	48	
Ba^2	7·5	(2) (3)
Pb^2	12·5	
Sr^2	9·9	(1)
Ca^2	12	
Mg^2	22·8	(1)
Co^2	24	

(*N.B.* For the pair Ba^2-Pb^2, comparison is made on the basis of their relative enrichment at the K′ sites in crystals.)

Data from Wager and Mitchell (1) 1951; Nockolds and Mitchell (2) 1948; Rankama and Sahama (3) 1950.

In each of these pairs, between which diadochy occurs in magmatic minerals, the observed enrichment is contrary to the prediction based on F values.

6. The Influence of Sulphur on Trace Element Distribution in Magmas

The distribution of some elements between crystals and melt is complicated by their tendency to combine with any sulphur present. Such elements are classed

as chalcophile by Goldschmidt. Forland and Weyl (1949) have shown that highly polarizing cations possessing non-noble gas electron configurations will combine preferentially with any sulphur in silicate melts, forming either discrete non-polar molecules, or precipitating as separate sulphide crystals. This process decreases the effective concentration of chalcophile cations in the melt and could complicate any treatment concerning the partition of such cations between silicate crystals and the magma.

However, the process is quantitatively unimportant in magmas except in the case of Cu^2 and Ag^1. Rankama and Sahama (1950) have shown that apart from these two, the "chalcophile" elements in magmas become predominantly incorporated in silicate minerals rather than sulphides. The reason for this is that the sulphur content of magmas is relatively very low, and nearly all of the sulphur combines with highly polarizing Fe^2 ions which are abundant. The small amount which is left is taken up mostly by the Cu^2 ions which possess greater polarizing power than Fe^2. Accordingly ions of B sub-group or transition elements behave as free cations in nearly all magmas.

7. The Behaviour of Individual Trace Elements in Magmas

In the following pages the behaviour of individual elements will be discussed in terms of the principles suggested previously. Detailed discussion will be restricted to the better-known trace elements and will be concentrated on elements whose behaviour is not readily explained on the basis of the Goldschmidt Rules.

Before commencing a detailed discussion, some remarks on the use of the term "camouflage" might be appropriate, since it is used rather frequently.

"Camouflage" as usually defined, refers to the diadochy between a major rock-forming element and a trace element. The trace element is said to be camouflaged by the major element. It often happens, however, that two or more major elements may occupy the same structural site in a crystal lattice, e.g., Mg^2-Fe^2 in olivine, Fe^3-Al^3 in pyroxene. When a trace element occurs in such a lattice site, the question arises as to whether it is camouflaged by one, or the other, or both major elements. Nearly always investigation shows that the trace element has entered the lattice at the expense of one of the major elements rather than the other. Thus, V^3 and Cr^3 enter lattice positions containing Al^3 and Fe^3 at the expense of Fe^3 whilst Co^2 enters Mg^2-Fe^2 positions at the expense of Fe^2. In the following pages, the term "camouflage" is restricted to the entrance of a trace element at the expense of a particular major element at a lattice site as in the above examples. Camouflage is therefore taken to indicate a relation between a trace element, and a particular major element, not simply between a trace element and a particular lattice site.

(a) *Copper*

Rankama and Sahama (1950) showed that a large part of the copper contained in most igneous rocks occurs as sulphides. However, Wager and Mitchell (1951) have demonstrated that during the earlier stages of crystallization of a basic magma, copper occurs free in the magma, and is able to become incorporated in silicate minerals. The copper occurs as Cu^1 and Cu^2. The Cu^1 (0·96 Å) is

camouflaged by Na^1 (0·98 Å) in plagioclase, whilst Cu^2 (0·72 Å) is camouflaged by Fe^2 (0·74 Å) in ferromagnesians. Their results prove that copper does not enter crystals as readily as Na^1 and Fe^2 and is therefore concentrated in residual magmas until a concentration is reached which is sufficient to precipitate $CuFeS_2$.

Such behaviour cannot be explained by the Goldschmidt Rules, since the radii of Cu^1 and Cu^2 are smaller than those of Na^1 and Fe^2. The reason for this behaviour must be sought in consideration of the bonding prevailing.

The electronegativity of Cu^1 is 1·8 compared to Na^1, 0·9. Therefore Cu^1-O bonds will be much more covalent than Na-O bonds and will therefore be considerably weaker because of the reasons put forward previously. The electronegativity of Cu^2 is 2·0, as compared with Fe^2—1·65, consequently Cu^2-O bonds will be much weaker than Fe^2-O bonds for the same reason. Because of the relative weakness of the Cu-O bonds, copper does not readily enter silicate minerals, and therefore accumulates in the residual magma, until a concentration sufficient to precipitate $CuFeS_2$ is reached.

(b) *Lead*

Lead (radius 1·2 Å) occurs in silicate structures mainly as the Pb^2 ion, and displays diadochic substitution with K^1 (1·33 Å). According to the Goldschmidt Rules, Pb^2 should be relatively concentrated in the early potash-bearing minerals, because of its high charge. However, in fact, lead does not enter the potash felspar lattice as readily as potassium and hence becomes concentrated in the residual magma. (Rankama and Sahama, 1950; Nockolds and Mitchell, 1948).

The electronegativity of Pb is 1·8 compared to 0·8 for K. Hence the Pb-O bonds in orthoclase and mica are very much more covalent than the K-O bonds and this has the effect of weakening them considerably. This explains why lead is not relatively concentrated in potash-bearing minerals, but tends to accumulate in residual magmas.

(c) *Manganese*

Manganese (radius 0·8 Å) occurs in magmas as the Mn^2 ion (Rankama and Sahama, 1950). It is camouflaged chiefly by Fe^2 (0·74 Å). Wager and Mitchell (1951) have shown that the tendencies of Fe^2 and Mn^2 to enter lattices are about equal. According to the Goldschmidt Rules, Mn^2 should not enter lattices as easily as Fe^2 because of its larger radius. However, the electronegativity of Mn^2 is 1·4 compared with 1·65 for Fe^2. Consequently the Fe-O bonds are more covalent, and therefore weakened. The weakening of the Fe-O bonds due to extra covalent bonding tends to compensate for its higher ionic bonding energy due to a smaller radius and hence the Mn-O and Fe-O bond energies are about equal. Accordingly they possess about the same tendency to enter crystals.

(d) *Nickel*

Present opinion regarding the geochemical behaviour of nickel is based largely upon the classic researches of Vogt (1923). Vogt brought forward an imposing array of data which appeared to show that the behaviour of nickel was due to its camouflage by magnesium. This opinion has since been widely accepted, indeed

the Ni-Mg diadochy is frequently cited as a perfect example of the camouflage principle. In the opinion of the author, this conclusion which was derived from Vogt's results is not justified; furthermore a consideration of some basic principles of crystal chemistry suggests that Ni^2 is unlikely to proxy extensively for Mg^2 in minerals. It is far more likely that Ni^2 enters crystal lattices at the expense of Fe^2 rather than Mg^2.

Vogt's conclusions may be summarized. He found that nickel in igneous rocks was contained mainly in olivine, followed next in importance by orthopyroxene and then clinopyroxene. Furthermore, he found that the greatest amount of nickel was contained in those minerals which were richest in magnesium. Nickel tended to occur in greatest abundance in the forsterite rich members of the olivine series, and decreased in amount as the content of iron increased, and the magnesium decreased. Similarly for the orthopyroxene and clinopyroxene. These findings have been reinforced by numerous subsequent geochemical studies by other workers.

A very complete study of the behaviour of nickel was carried out by Wager and Mitchell (1951) on the Skaergaard Intrusion. The importance of their results lies in the fact that they were able to estimate the amount of nickel in the magma from which the nickel-bearing minerals were crystallizing. Their results showed conclusively that the smaller amounts of nickel in the later olivines and pyroxenes were caused by a decrease in the concentration of nickel in the residual magma, and were not related to the smaller amount of magnesium present in the minerals. In fact, in the case of the pyroxenes, the tendency of nickel to enter increased as the content of magnesium decreased. The decrease in nickel content of the magma as fractionation progressed was due to its entry into early crystals in excess of the amount present in the magma. At an intermediate stage of differentiation, nickel is almost completely removed.

The fact that Ni is always relatively enriched in early crystals does not prove that it is being camouflaged by Mg. The sympathetic variation displayed by these elements could just as well be due to the fact that Ni also is enriched in early crystals relative to Fe. If Ni was being camouflaged by Fe, and displaying a high relative enrichment towards that element, the observed relationships could be equally well explained.

It is therefore clear that the relationships observed by Vogt and substantiated by other workers do not prove whether Ni is camouflaged by Mg or by Fe. One item of Vogt's data, however, is in contradiction with his conclusions.

Vogt observed that when olivine and orthopyroxene of the same rock are compared, the olivines are always richer in nickel than the orthopyroxenes. Recently Ramberg and De Vore (1949) have demonstrated that when olivines and orthopyroxenes from the same rock are compared, the olivines are usually richer in Fe relative to Mg than the orthopyroxenes. If the Ni was being camouflaged by Mg it is to be expected that the orthopyroxene would be richer in nickel than the coexisting olivine, whereas the opposite is true, suggesting that Ni follows Fe rather than Mg.

Goldschmidt (1944) has claimed that the observed relative concentration of Ni in Mg-bearing minerals is due to the Ni-O bond being stronger than the Mg-O

bond because of its more covalent character. However this argument cannot be accepted since it has been previously shown that the effect of increased covalent bonding is to weaken the bond.

A study of the crystal chemistry of Ni, Fe, and Mg compounds strongly suggests that Ni is camouflaged by Fe rather than Mg in silicates. If Ni were substituting for Mg in olivine, the compound Ni_2SiO_4 must have a much higher melting point than Mg_2SiO_4 (1,890°C) in view of the strong enrichment of Ni relative to Mg in the early crystals. This would contradict a fundamental law of crystal chemistry which has been dealt with earlier—namely that substitution of the cation of a B sub-group or transition element for that of an A sub-group element in any structure weakens the structure and results in a lower melting point due to an increase in the covalent component in the bonds. The electronegativity of Ni is 1·7 compared with 1·2 for Mg; consequently the Ni-O bonds possess a much greater covalent component. Furthermore, additional weakening of the bond comes about since the ionic radius of Ni^2 (0·69 Å) is greater than that of Mg^2 (0·66 Å).

The truth of these relationships is well displayed by the oxides. The melting temperature of MgO is 2,800°C compared with 1,990°C for NiO. It is therefore clear that MgO would be concentrated in the early crystallates relative to NiO in an oxide melt. Since the melting of both Mg_2SiO_4 and Ni_2SiO_4 involves the breaking of Mg-O and Ni-O bonds these figures are particularly revealing. It is concluded therefore that the influence of a larger covalent component in the Ni-O bond must weaken it relatively to the Mg-O bond and consequently Ni is not camouflaged extensively by Mg in silicate minerals.

However, the situation with regard to the Ni^2-Fe^2 diadochy is completely different. The electronegativities of Fe and Ni are almost identical (1·65 and 1·7). Consequently both form bonds with covalent components of the same magnitude. Under these circumstances the smaller size of the Ni^2 ion (0·69 Å) compared with Fe^2 (0·74 Å) will facilitate its preferential entry into early crystals because of its higher ionic bonding energy. The melting points of the oxides show this effect. FeO—1,420°C, NiO—1,990°C. It is therefore apparent that the Ni-O bond is stronger than the Fe-O bond and consequently nickel will be relatively concentrated in the early crystals.

Therefore it is concluded that the dominant geochemical characteristic of nickel is its camouflage by ferrous iron in silicate crystals. This camouflage is such that Ni^2 is highly concentrated relative to Fe^2 in early crystals giving rise to an apparent camouflage relationship between Ni^2 and Mg^2 which is, however, illusory.

(e) *Tin*

Tin occurs in magmas as Sn^2 and Sn^4 (Rankama and Sahama, 1950). It will be shown in Part II that Sn^4 does not readily enter silicates but accumulates in residual magmas. The behaviour of Sn^2 must now be considered. Sn^2 has a radius of 0·93 Å compared with 0·99 Å for Ca^2; hence it might be expected that Sn^2 would be camouflaged in Ca-bearing minerals, entering into early fractions in excess of Ca, and thus becoming impoverished in the magma. However, the behaviour of Sn^2 is contrary to expectation and the reason is to be found in the type

of bond it forms with oxygen. The electronegativity of Sn^2 is 1·65 compared with 1·0 for Ca^2. It is therefore clear that Sn-O bonds must be much more covalent and therefore weaker than Ca-O bonds. This is seen from the thermal behaviour of the oxides. SnO is decomposed at about 700°C, whereas CaO melts at 2,570°C. Because of the relative weakness of Sn^2-O bonds, Sn tends to remain in residual magmas.

(f) *Vanadium*

Vanadium occurs in magmas principally as V^3. However, a small amount of V^5 occurs, which, as will be shown in Part II, becomes concentrated in residual pegmatitic magmas. With regard to V^3 however, the situation is different. Wager and Mitchell (1951) have shown that V^3 (0·74 Å) is camouflaged by Fe^3 (0·64 Å) during the fractionation of a silicate magma. Contrary to the Goldschmidt Rules, however, V^3 displays a high degree of preferential concentration relative to Fe^3 so that V^3 is rapidly removed from the magma as soon as Fe^3 is precipitated in any abundance (in magnetite). This behaviour is fully explained by the smaller electronegativity of V^3 (1·35) compared to Fe^3 (1·8).

(g) *Chromium*

Chromium occurs in magmas as Cr^3. The results of Wager and Mitchell (1951) show that Cr^3 is camouflaged by Fe^3 during the fractionation of a silicate magma. Chromium displays a very high degree of preferential concentration relative to Fe^3 in minerals containing that ion, and is rapidly removed from the magma. Such behaviour cannot be accounted for on the basis of ionic radii, which are similar—Fe^3 (0·65 Å); Cr^3 (0·64 Å). However, it is fully explained by the smaller electronegativity of Cr^3 (1·6) compared to Fe^3 (1·8).

(h) *Scandium*

During magmatic crystallization, scandium preferentially enters the early ferromagnesian minerals occupying the Mg-Fe positions, thereby becoming impoverished in residual magmas (Rankama and Sahama, 1950). The radius of Sc^3 is 0·81 Å compared to Mg^2 (0·66 Å), and Fe^2 (0·74 Å). It is probable that Sc^3 becomes preferentially concentrated at the expense of Fe^2 rather than Mg^2. Although Sc^3 possesses a higher charge than Mg^2 its radius is considerably larger, and its electronegativity is also greater ($E_{Sc} = 1{\cdot}3$, $E_{Mg} = 1{\cdot}2$). Both these factors would tend to retard the entry of Sc^3 into crystals compared to Mg^2. However, the radius of Sc^3 is much closer to that of Fe^2, and the electronegativity of Sc^3 is much smaller than that of Fe^2 ($E_{Fe} = 1{\cdot}65$). Consequently scandium possesses a far greater tendency to enter a suitable lattice site than iron, and this tendency dominates its behaviour.

A certain amount of scandium becomes concentrated in residual pegmatitic magmas. The reason for this apparently anomalous behaviour will be discussed in Part II.

(i) *The rare earths*

The ionic radii of the trivalent rare earths vary between 0·85 Å and 1·14 Å, consequently diadochy would be expected with Ca^2 (0·99 Å). That this diadochy

occurs is well known; however, according to the Goldschmidt Rules, the rare earths should become preferentially concentrated in early Ca minerals because of their high charge, thereby becoming impoverished in residual magmas. This does not occur, and the rare earths become concentrated in residual magmas. This behaviour is explained by the electronegativity relationships, since the electronegativities of the rare earths ($E_Y = 1{\cdot}2$, $E_{La} = 1{\cdot}1$, $E_{Pr} = 1{\cdot}1$, $E_{Ce} = 1{\cdot}05$) are greater than that of Ca ($E_{Ca} = 1{\cdot}0$). These differences in electronegativity are not large, yet they are apparently sufficient to offset the effect of the higher charge on the trivalent rare earth ions.

Wickman (1943) has suggested that the relative reluctance of rare earth ions to preferentially substitute for Ca^2 in silicates is caused by difficulty in attaining electrical neutrality. It is difficult to see why this should be so, since the difference in charge is only unity—neutrality can easily be maintained by the substitution of an AlO_4^{-5} group for SiO_4^{-4}. Sc^3 is captured by Fe^2 in pyroxenes, and there is apparently no difficulty about maintaining electrical neutrality; it might therefore be expected that the trivalent rare earths should substitute for Ca^2 in pyroxene with equal facility.

(j) *Zinc*

The ionic radii of Zn^2 and Fe^2 are similar (0·74 Å), consequently zinc is camouflaged in minerals containing ferrous iron. Wedepohl (1953) demonstrated that the content of Zn in basic rocks is much greater than in acidic rocks; however the Zn/Fe ratio appears to increase during differentiation. The latter finding is in full accord with the results of Lundegardh (1948).

Haissinsky (1946) gives the electronegativity of Zn^2 as 1·5, compared to 1·65 for Fe^2. These values do not explain the above behaviour. Recently, however, Altshuller (1954) has recalculated the electronegativity of Zn from dissociation energy data and has obtained the value 1·7, making zinc more electronegative than iron. This value is to be preferred since it is consistent with the relative ionization potentials ($I_{Fe^2} = 16{\cdot}24$ volts; $I_{Zn^2} = 17{\cdot}95$ volts).

The tendency of zinc to become concentrated in residual magmas relative to ferrous iron is thus fully explained by its higher electronegativity.

(k) *Other elements*

There is little detailed knowledge of the behaviour of Ag^1, Cd^2, Hg^2, Sb^3, and Bi^3 during magmatic crystallization. In a general way, however, it is known that these ions tend to become concentrated in residual granitic magmas, finally giving rise to ore deposits genetically related to these magmas (Rankama and Sahama, 1950). This behaviour is fully in accord with the electronegativity relationships shown in Table 3. In each case, the electronegativity of the trace element is considerably greater than that of its potential host in magmatic minerals.

8. Summary

The influence of electronegativity upon the behaviour of trace elements during magmatic crystallization has been discussed, and the following general rule suggested—

Whenever diadochy in a crystal is possible between two elements possessing

Table 3. Summary of trace element behaviour

A			*B*		
Element	*Ionic radius* (Å)	*Electro-negativity*	*Element*	*Ionic radius* (Å)	*Electro-negativity*
Na^1	0·97	0·9	Ni^2	0·69	1·7
Cu^1	0·99	1·8	Fe^2	0·74	1·65
Fe^2	0·74	1·65	Co^2	0·72	1·7
Cu^2	0·72	2·0	Fe^2	0·74	1·65
Fe^2	0·74	1·65	K^1	1·33	0·8
Zn^2	0·74	1·7	Rb^1	1·47	0·8
K^1	1·33	0·8	Mg^2	0·66	1·2
Pb^2	1·20	1·6	Li^1	0·68	1·0
Ca^2	0·99	1·0	Ba^2	1·34	0·85
Sn^2	0·93	1·65	K^1	1·33	0·8
V^3	0·74	1·35			
Fe^3	0·64	1·8			
Cr^3	0·63	1·6			
Fe^3	0·64	1·8			
Sc^3	0·81	1·3			
Fe^2	0·74	1·65			
Ca^2	0·99	1·0			
(Rare earth)^3	0·85–1·14	1·05–1·2			
K^1	1·33	0·8			
Ag^1	1·26	1·8			
Ca^2	0·99	1·0			
Cd^2	0·97	1·5			
Ca^2	0·99	1·0			
Hg^2	1·10	1·9			
Fe^2	0·74	1·65			
Sb^3	0·76	1·8			
Ca^2	0·99	1·0			
Bi^3	0·96	1·8			

N.B. In each case, the element which is preferentially concentrated in crystals relative to the other is placed first.

Column A gives examples of diadochy controlled by the electronegativity rule.

Column B gives examples of diadochy controlled by the Goldschmidt Rules.

appreciably different electronegativities, the element with the smaller electronegativity is preferentially incorporated.

In most cases, the difference in electronegativity required before elements obey the above rule is about 0·1.

When diadochy occurs between elements possessing similar electronegativities, the Goldschmidt Rules are usually applicable (although some exceptions occur). Thus, the smaller of the two competing ions is usually preferentially incorporated in crystals provided the charges are equal. Similarly, the more highly-charged of two competing ions is preferentially enriched.

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Book reviews

K. RANKAMA: **Isotope Geology.** Pergamon Press Ltd., 1954. 535 pp. 75s.

THIS book is the first in English on a general field* for which the author proposes the term "Isotope Geology": this is defined as, "investigation of geological phenomena by means of stable and unstable isotopes of elements and of changes in their abundance." The geological implications and applications are many, and include the determination of geological age, generation of heat by radioactivity, measurement of paleotemperatures, origin of coal, calcite, etc. The appearance of "Nuclear Geology" (H. FAUL, Ed.—John Wiley, New York) close on the heels of "Isotope Geology," covering some of the same field, together with the probability of a third book, all testify to the intense activity which has developed recently in the field covered by isotope geology.

The book begins with several chapters addressed mainly to geologists, and is intended to provide "an account of the physics and chemistry of nuclides and of the principal methods used in research in isotope geology." This part (Part 1) is titled "Physics and Chemistry of Nuclides," and includes chapters on Atoms, Nuclei, and Nuclides; Isotopy; Mass Analysis; Radioactivity; Properties of Nuclear Radiation, Isotope Fractionation, and others. Part 2 represents the heart of the book, and is titled "Natural Science of Nuclides." Here a chapter is devoted to each element, and these are arranged according to atomic number. The enormous differences in chapter length reflect the differences in the amount of research which has been carried out on each element; whereas considerable literature has grown around certain elements, a few are likely to remain insignificant, either because they are stable or because they have only one isotope; or, if they have more, are not likely to show observable fractionation. Carbon has been investigated more thoroughly than any other element, and in a 53-page-long chapter RANKAMA lists some 330 or so $^{12}C/^{13}C$ ratios, and the reviewer is aware of another 100 which are about to be published. Oxygen, sulphur, and lead come next, followed by several elements such as Si, Mg, V, Ti, and B.

With the exception of carbon and a few of these other elements, none has been intensely investigated with respect to natural variation of isotopes, and this whole vast field is open to research. RANKAMA points out that fractionation has been observed in surprisingly heavy elements and may even be detected at masses as high as about 200, as in mercury, for example. Observable fractionation rests ultimately on sensitivity of mass measurements. Of more immediate analytical concern, however, is the need to remedy systematic differences between different laboratories. Thus, for example, after considering the measurements of THODE and OSBERGHAUS on boron (Chapter 15), RANKAMA finds that results cannot be compared, and concludes: "this discrepancy emphasizes the importance of referring the measurements of the isotopic composition of the various elements in Nature to common standards."

An interesting literature has grown around the isotope data of lead (all sources—from highly active minerals, as well as ores and meteorites) which, because of its various implications, has become almost a subject of its own; in fact, the half-serious and somewhat cacophonous "plumbology" is sometimes used in conversation as a useful term to cover all of these aspects. RANKAMA rightly attempts to define and distinguish various leads (primal, ordinary, radiogenic, and primary), but the distinction between ordinary and primary may seem ambiguous is some respects.

RANKAMA refers to the difficulty of one individual attempting to cover the literature completely; this is so, but his literature coverage is nevertheless unusually thorough, and some 1,244 references appear in the bibliography. Several references to private or personal communications testify to the author's efforts in attempting to keep abreast of the investigations. The

* Certain aspects of this general field have recently been covered; for example, "Non-radiogenic isotopes in geology: a review," by EARL INGERSON, *Bull. Geol. Soc. Amer.* **64,** 301 (1953), and Radiactividad y geofisica, by J. M. LÓPEZ DE AZCONA (*Bol. Inst. Geol Min. Espana*, LXIII, 303 pp., 1951). The Report of the Committee on the Measurement of Geologic Time (National Research Council, Washington) provides an exhaustive annual bibliography covering aspects of radioactivity which are of significance to geological age and earth-heat considerations; recent volumes include brief discussions on natural variations of isotopes in geological materials.

field is growing rapidly, and it is hoped that investigators will comply with the author's request for reprints for the purpose of the preparation of either supplements or a second edition. Some pertinent papers which are not referred to in the text are:

EIDINFF, M. L., PERRI, G. C., KNOLL, J. E., MARANO, B. J., and ARNHEIM, J.; The fractionation of hydrogen isotopes in biological systems. *J. Amer. Chem. Soc.*, **75,** 248–9 (1953).

IKAUNICKS, YA. YA.; Kinematics and distribution in space of carbon stars. *Izvest. Akad. Nauk. U.S.S.R., Ser. Fiz.*, **15,** 487–95 (1951) (Discusses C^{12}/C^{13} ratios in stars).

NICOLAYSEN, L. O., ALDRICH, L. T., and DOAK, J. B.; Age measurements on African micas by the strontium-rubidium method. *Trans. Amer. Geophys. Union*, **34,** 342 (1953).

PATTERSON, C., TILTON, G., and INGHRAM, M. G.; Abundances of uranium and the isotopes of lead in the earth's crust and meteorites. *Bull. Geol. Soc. Amer.*, **64,** 1461 A. (1953). For more recent data in this respect see "Nuclear Geology" (FAUL, ED.)

REUTERSWÄRD, C.; The isotopic abundance of K^{40}. *Ark. Fysik*, **4,** 203–205 (1952)

SHAIN, G. A., and GAZE, V. F.; Ratio of the concentration of the isotopes of C^{13} and C^{12} in stellar atmospheres. *Uspekhi Fiz. Nauk. U.S.S.R.*, **43,** 3–10 (1951).

TAMBUNINO, S. M., and STELLA, A.; Radioactivity of Etna lavas. *Nuovo Cimento*, **9,** 1044–1053 (1952).

In the preface RANKAMA states that research on isotope geology has been conducted chiefly by physicists and chemists, and that he sincerely hopes that "this volume is able to help the geologist toward the realization of the vast possibilities offered by the application of isotope research to a variety of geological problems." The book certainly fulfils this hope, and those seeking either general information in the field of isotope geology, a thorough reference source, or a guide to the many problems awaiting investigation, will find it invaluable.

L. H. AHRENS

ALFRED HARKER; **Petrology for Students. An introduction to the study of rocks under the microscope.** 8th ed., revised by C. E. TILLEY, S. R. NOCKOLDS, M. BLACK. Cambridge University Press, 1954. 18s.

IT is a great pleasure to see that HARKER's little book with its simple and lucid approach to petrography is again available for students. The book has been authoritatively revised and brought up to date but not altered in character. The drawings of the microscopic appearance of rocks which were an important feature of the original book, are unchanged and will still provide the student or research worker with the best example to follow in his own attempts at line illustration.

The book is really a petrography or description of the igneous, sedimentary, and metamorphic rocks. The scheme of classification of the igneous rocks is HARKER's own combination of the earlier ones of ROSENBUSCH and BRÖGGER; in it rock groups are not defined by particular characters or quantitatively, but by an aggregate of their presumed essential characters, that is characters which are believed to be of genetic significance. In the reviewer's opinion, HARKER's treatment of the classification and nomenclature of the igneous rocks is still the most objective of the simpler classifications available. A geochemist wishing to know something of the mineralogical classification of rocks and their appearance under the microscope will find this classic little work an ideal introduction.

L. R. WAGER

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AHRENS, L. H. (1952) *Geochim. et Cosmochim. Acta*, **2**, 168.

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